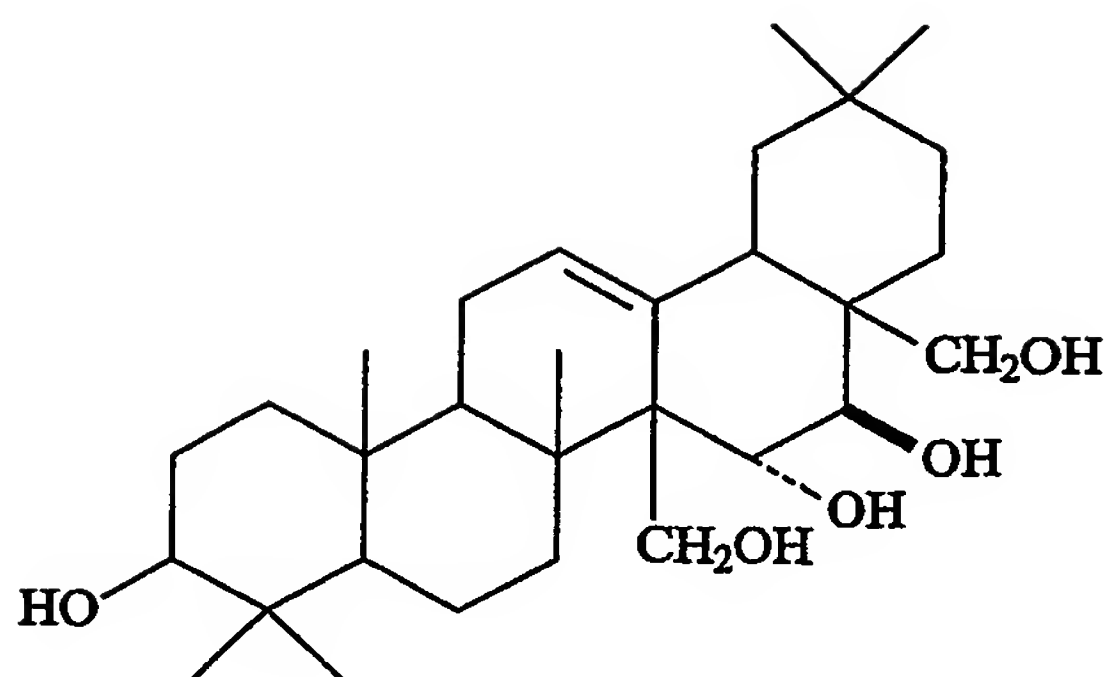
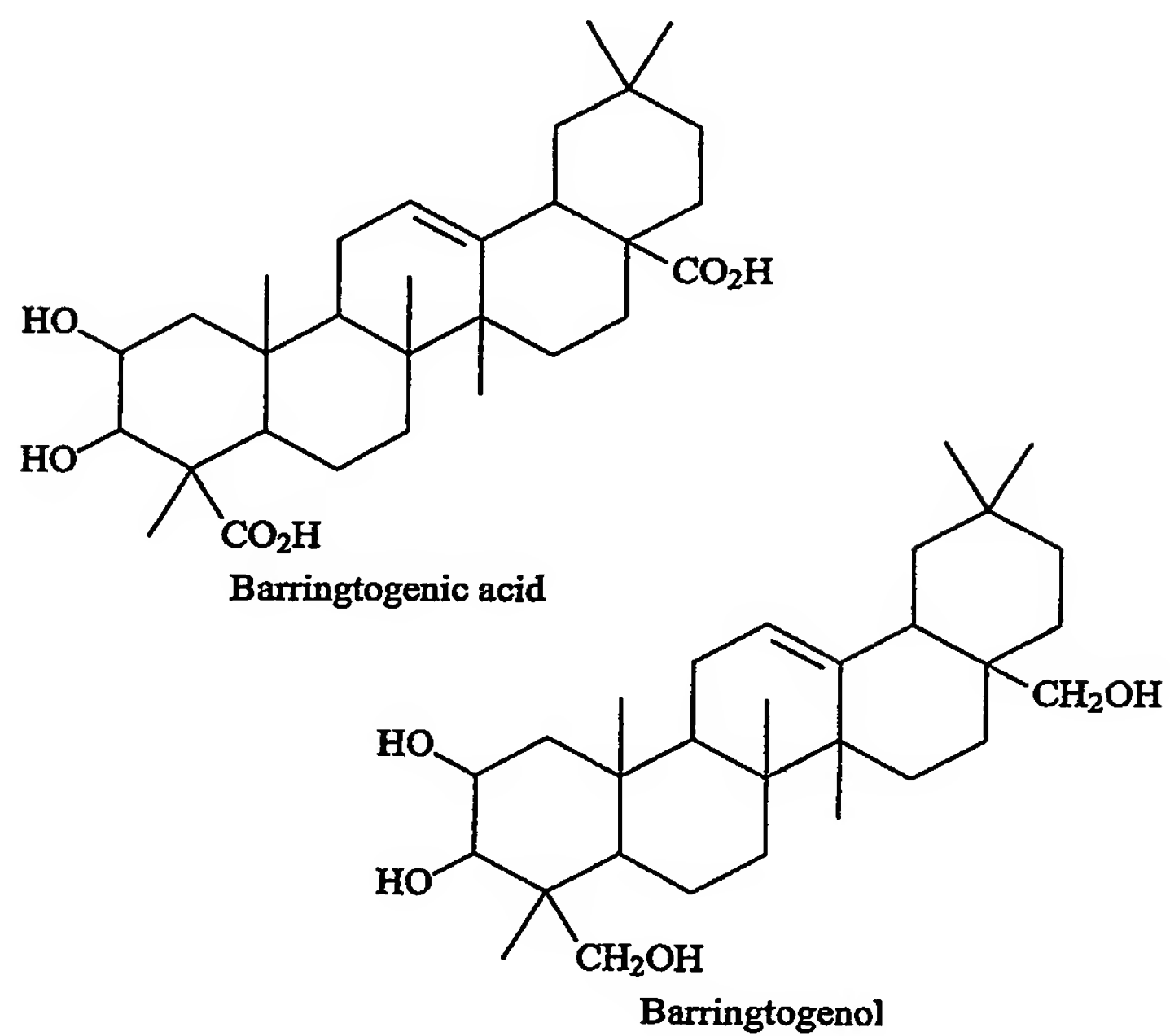
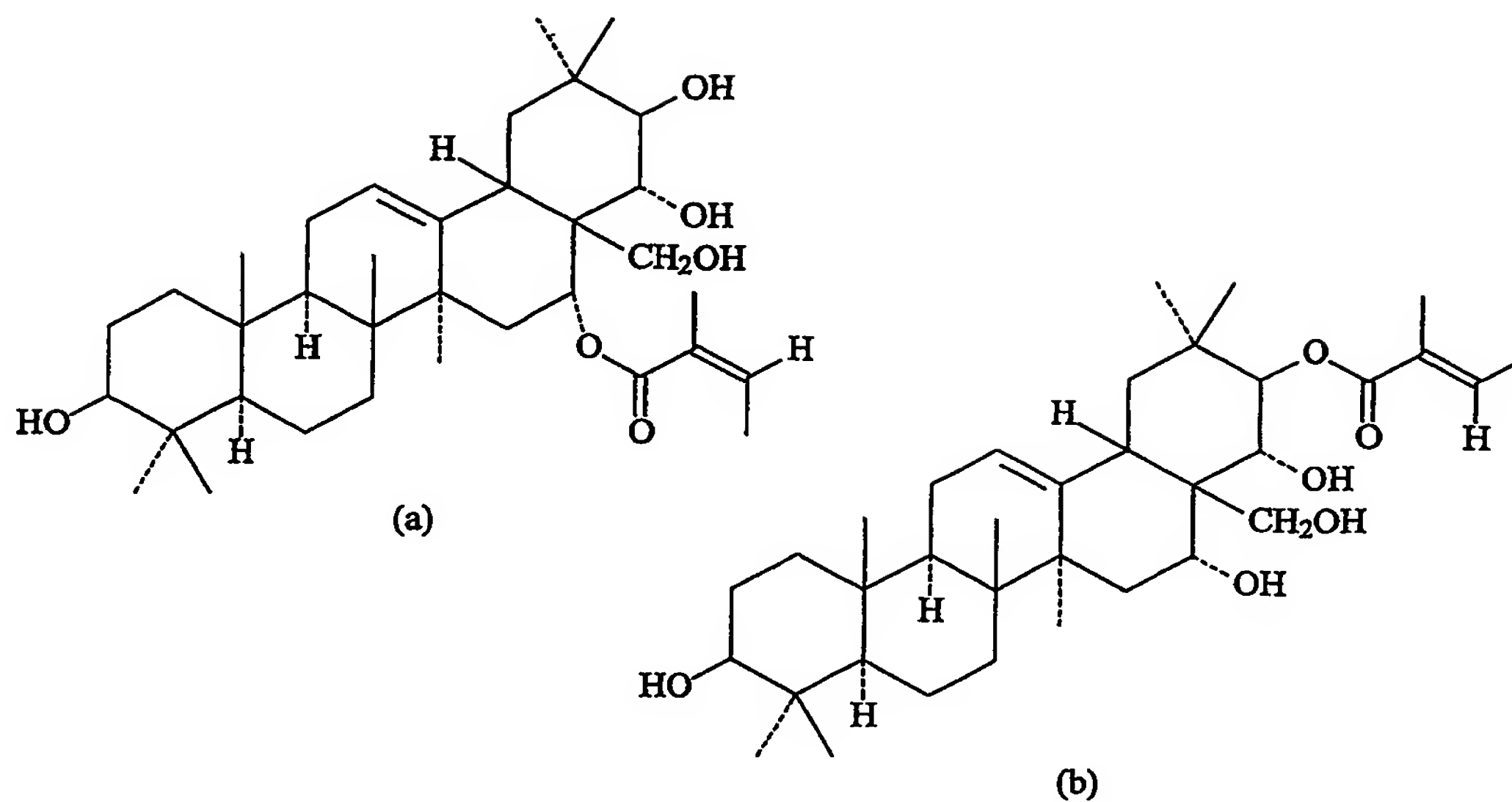
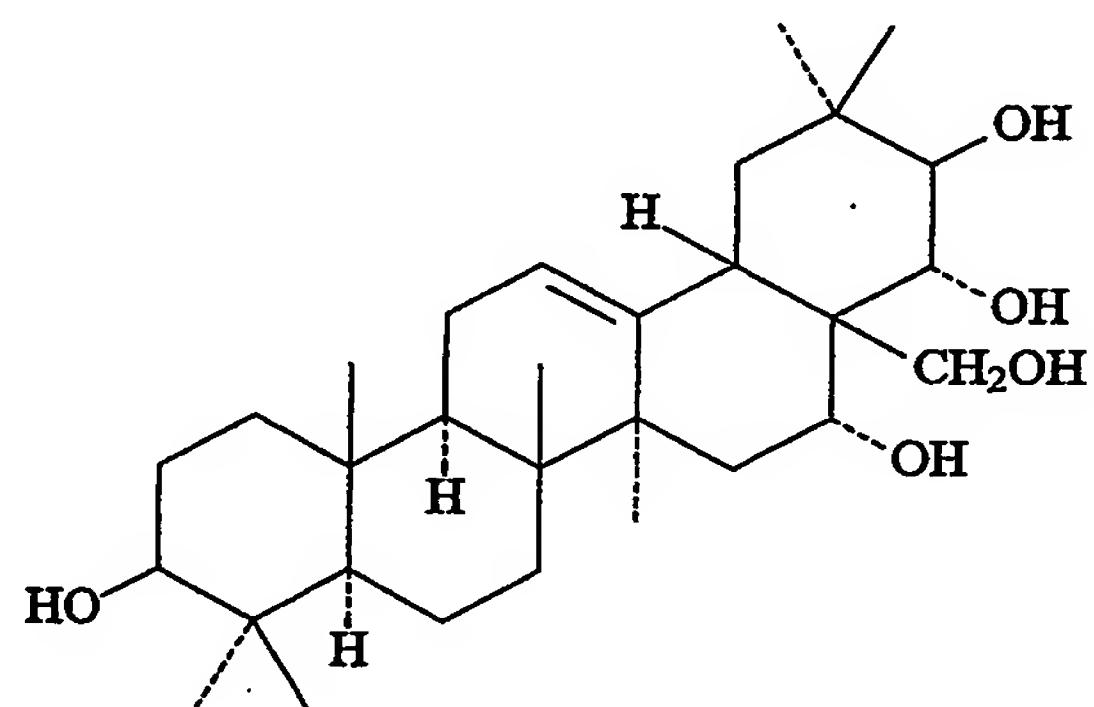
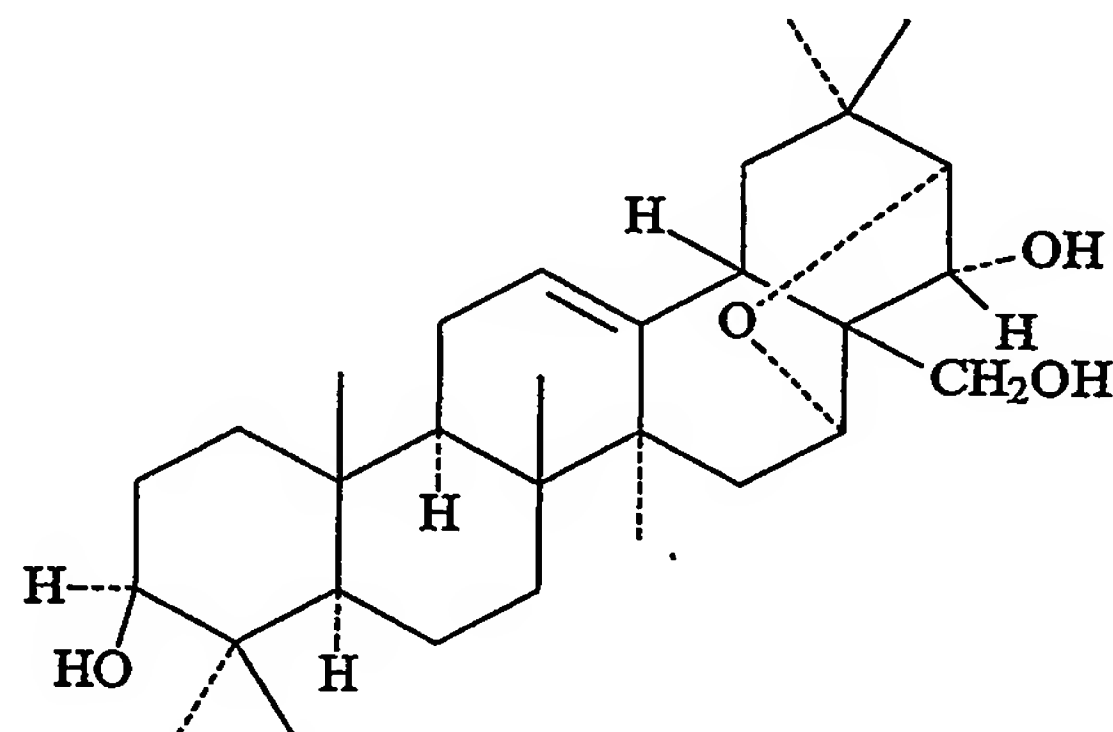


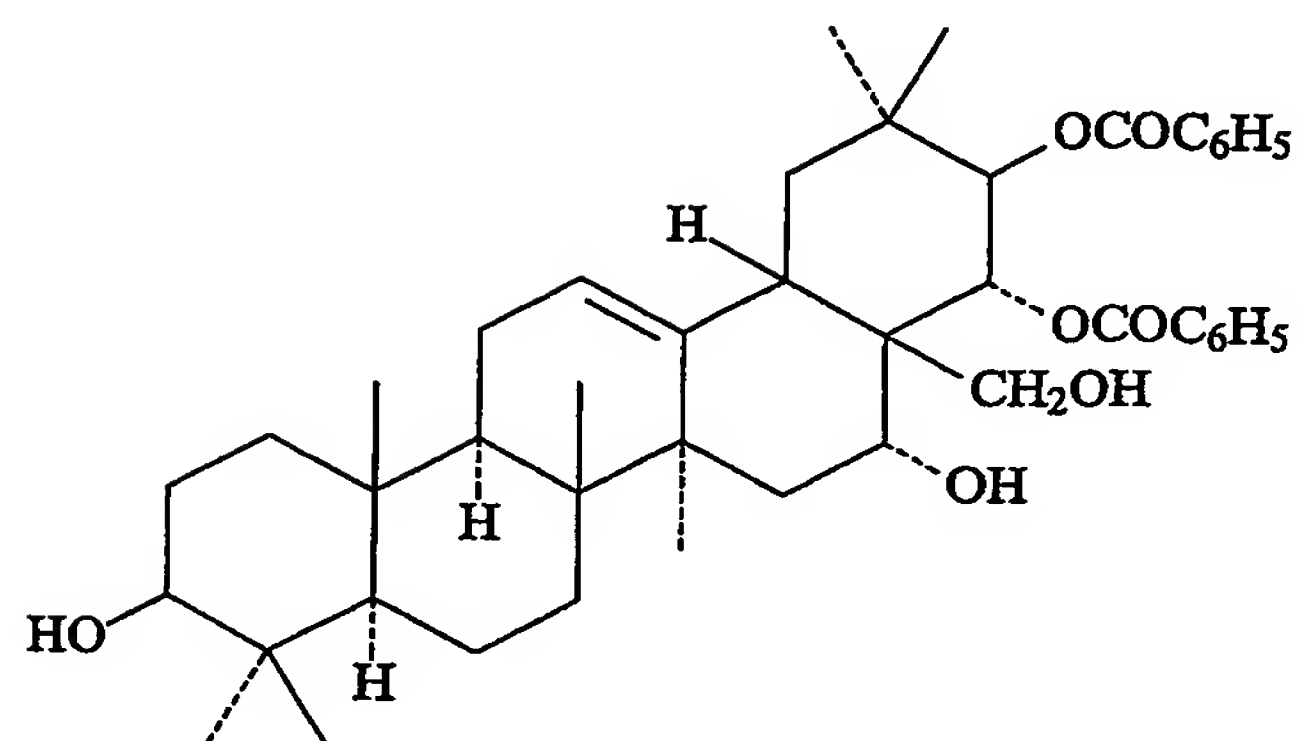
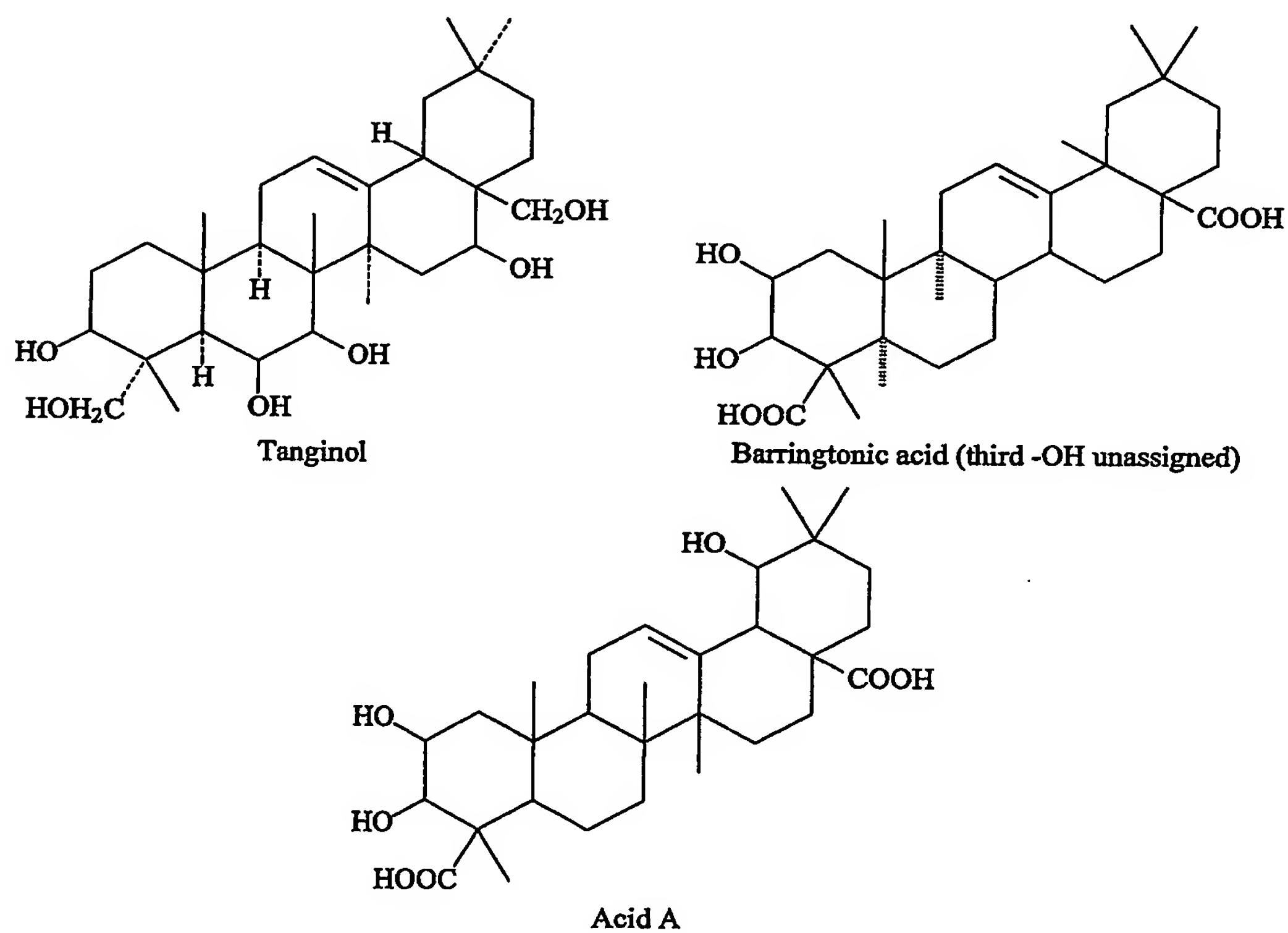
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**FIG 1.** A<sub>1</sub>-Barringenol**FIG 2.** The structure of barringtogenic acid and barringtogenol

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**FIG 3** (a) Initial and (b) revised structures of barringtogenol B**FIG 4** Barringtogenol C**FIG 5** – Barringtogenol D

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**FIG 6 – Barringtogenol E****FIG 7 – Compounds from *B. acutangula***

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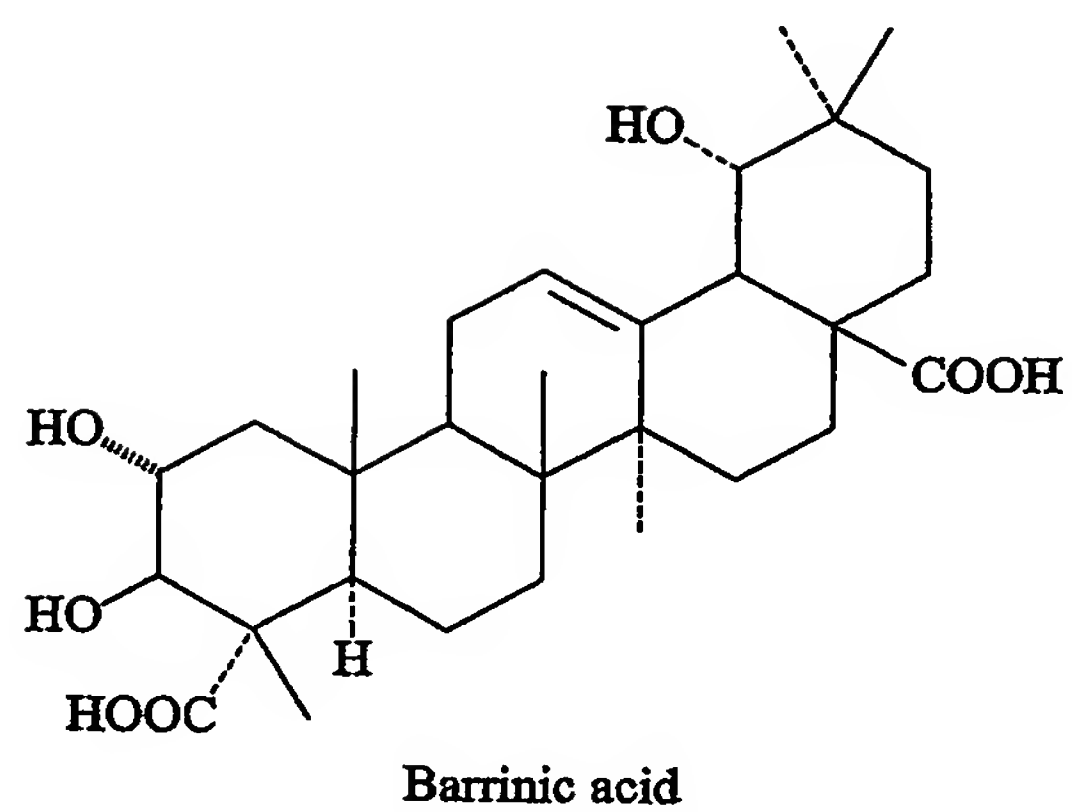
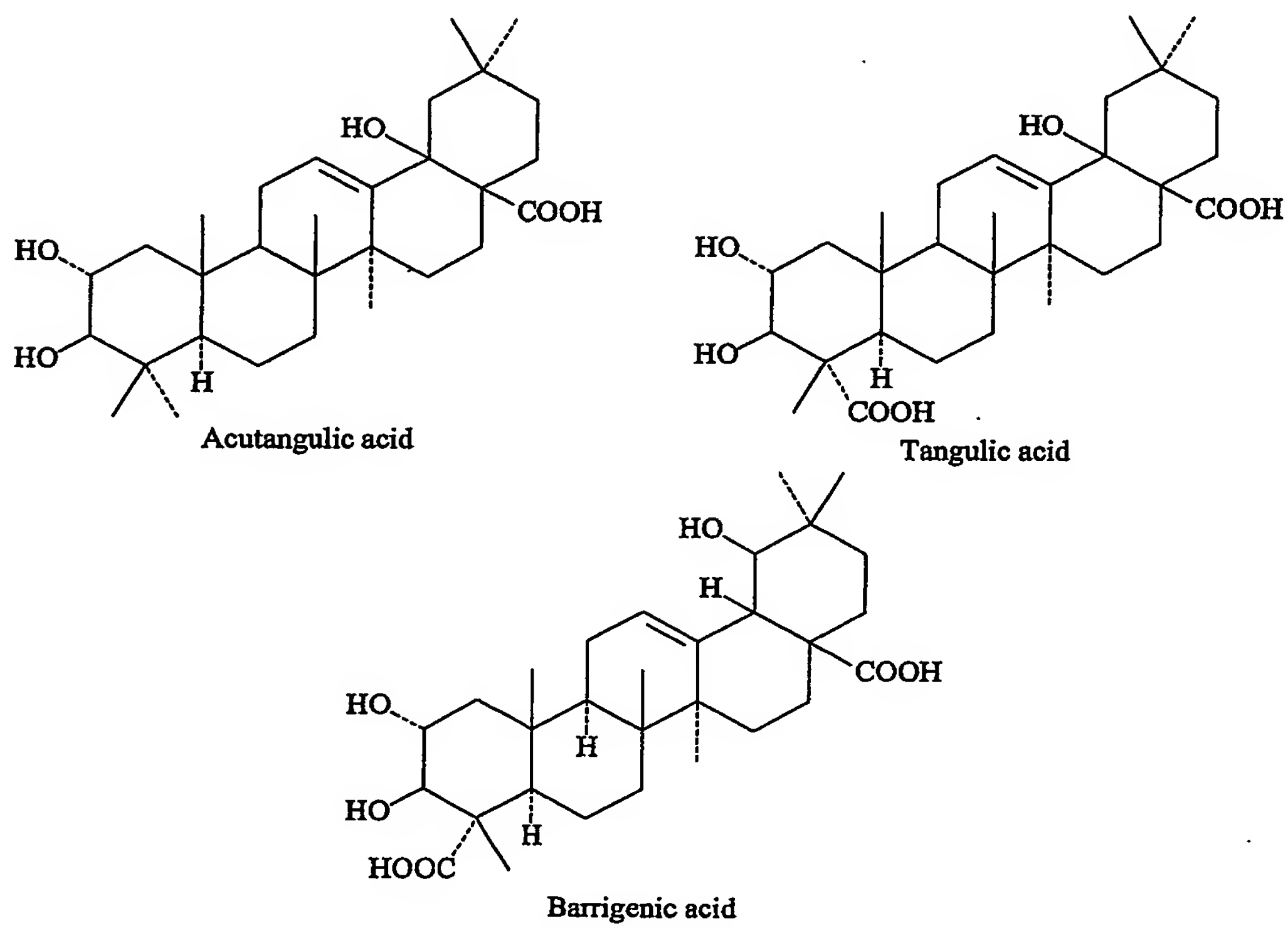
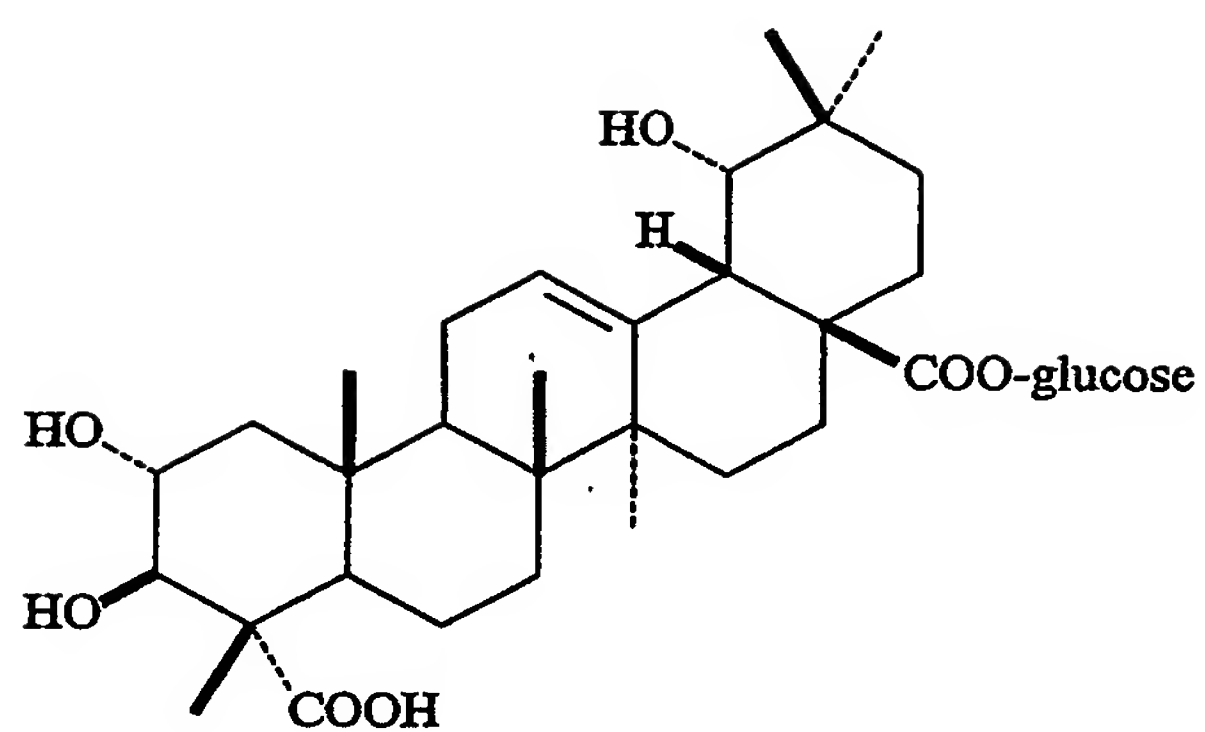


FIG 8. Barrinic acid

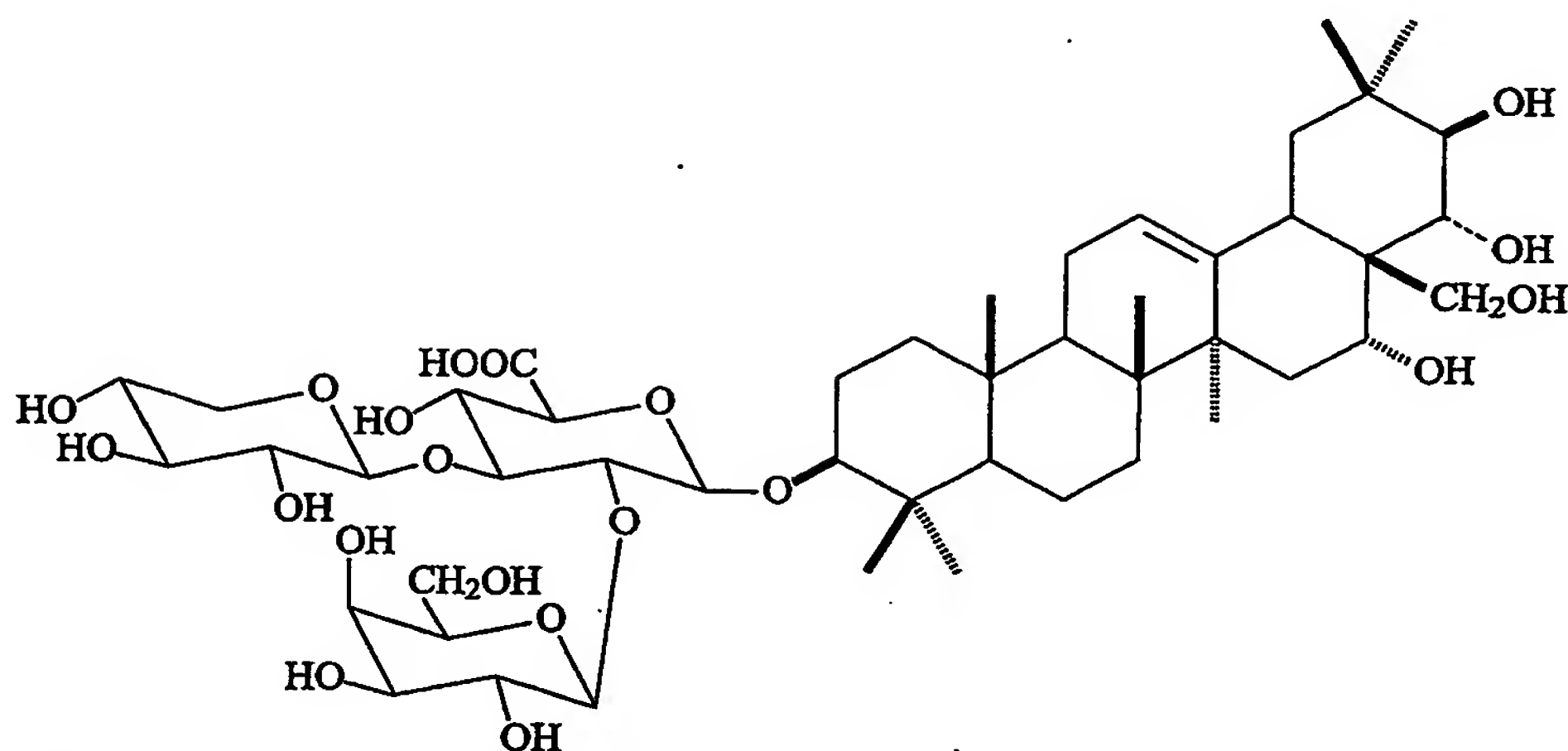
FIG 9 – Compounds from *B. acutangula*

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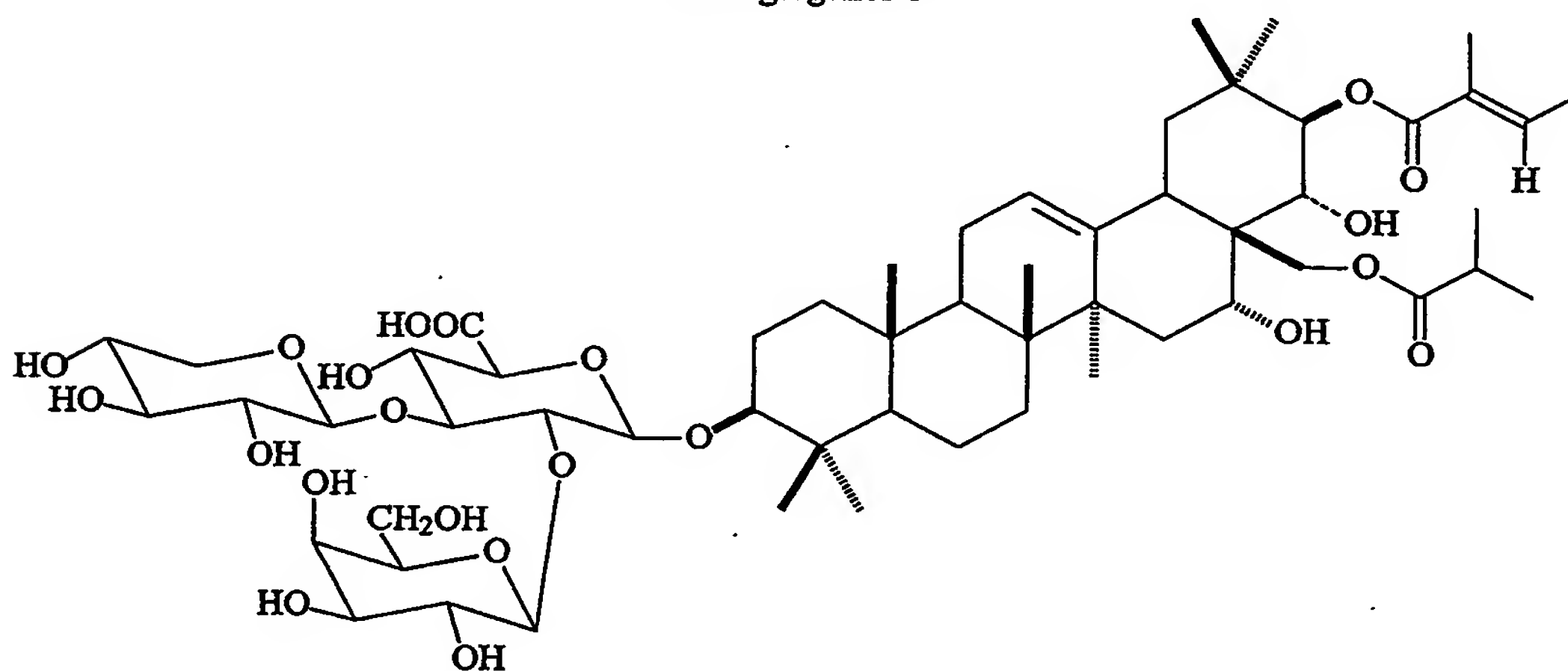


**FIG 10** -  $2\alpha,3\beta,19\alpha$ -trihydroxy-olean-12-ene-dioic acid 28-O- $\beta$ -D-glucopyranoside from the seeds of *B. acutangula*

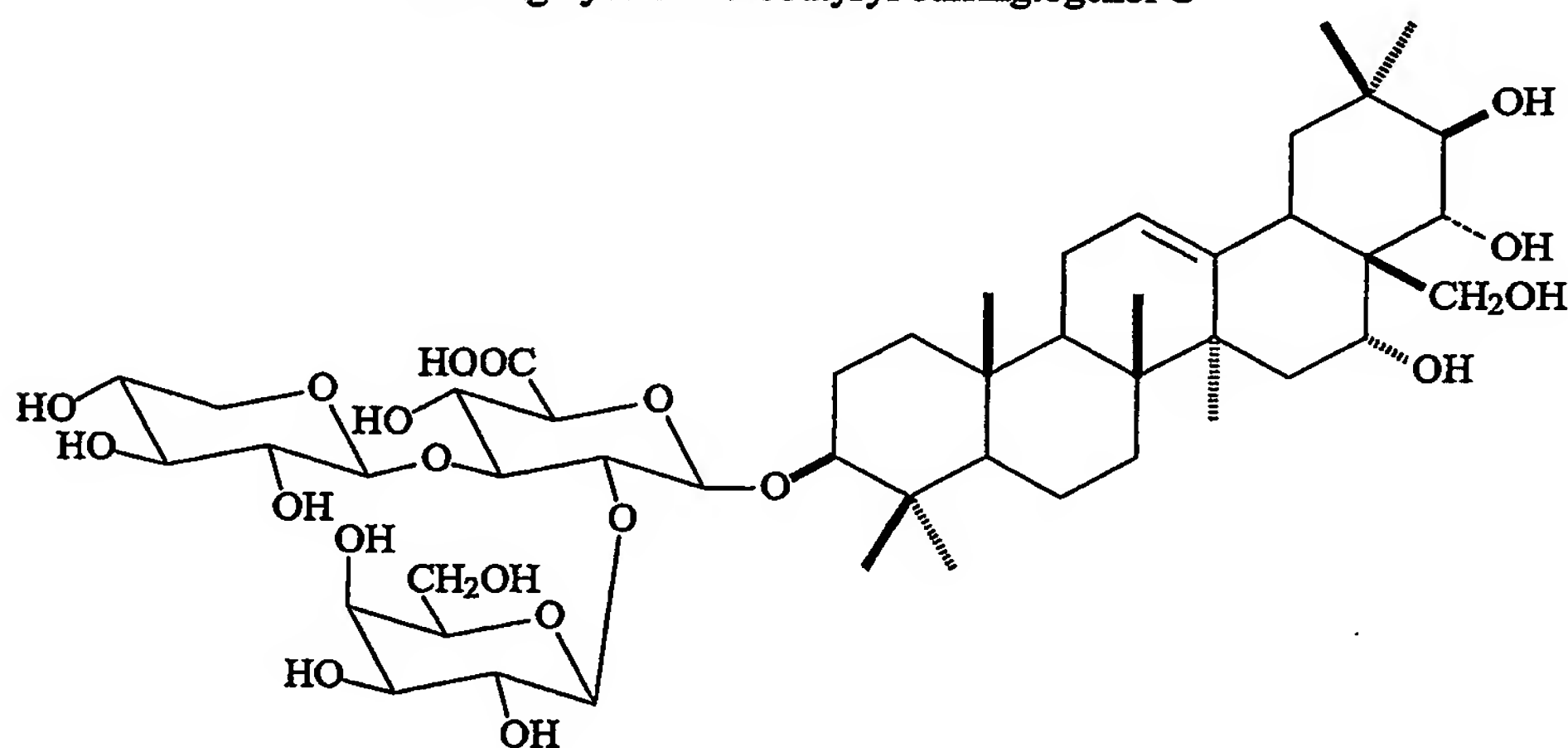
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Barringtonside A = 3-O- $\beta$ -D-xylopyranosyl(1 $\rightarrow$ 3)-[ $\beta$ -D-galactopyranosyl(1 $\rightarrow$ 2)]- $\beta$ -D-glucuronopyranosyl  
barringtonenol C



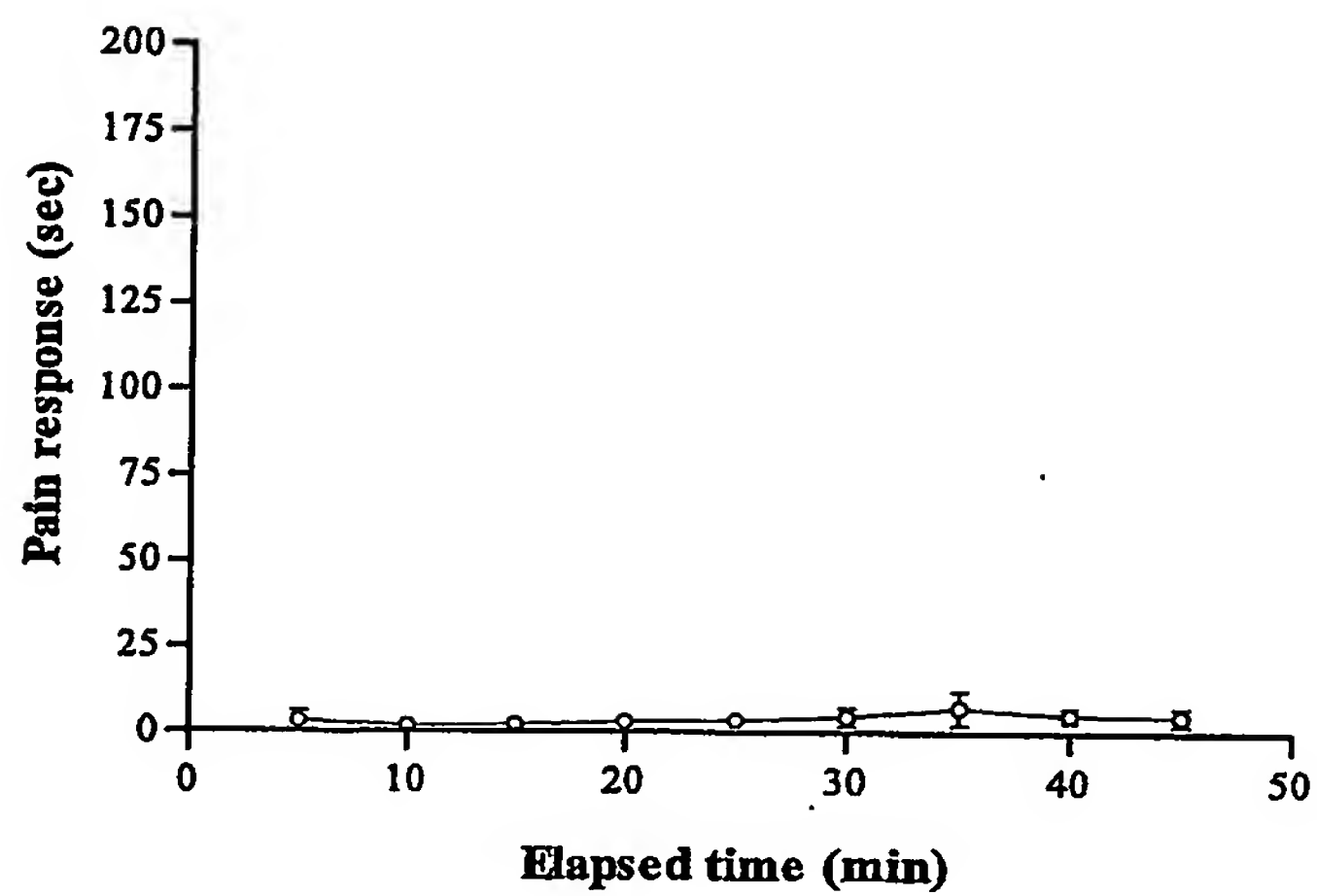
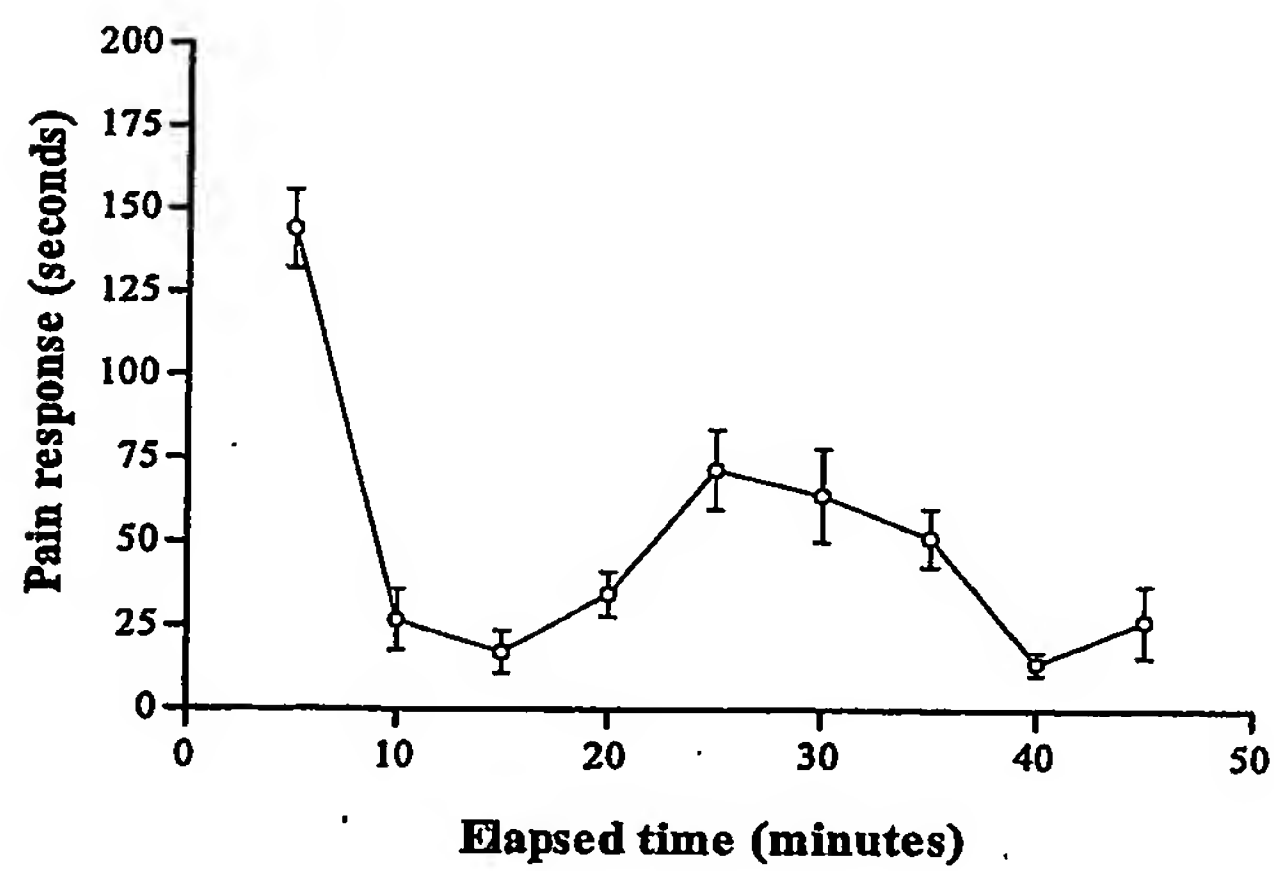
Barringtonside B = 3-O- $\beta$ -D-xylopyranosyl(1 $\rightarrow$ 3)-[ $\beta$ -D-galactopyranosyl(1 $\rightarrow$ 2)]- $\beta$ -D-glucuronopyranosyl  
-21-O-tigloyl-28-O-isobutyryl barringtonenol C

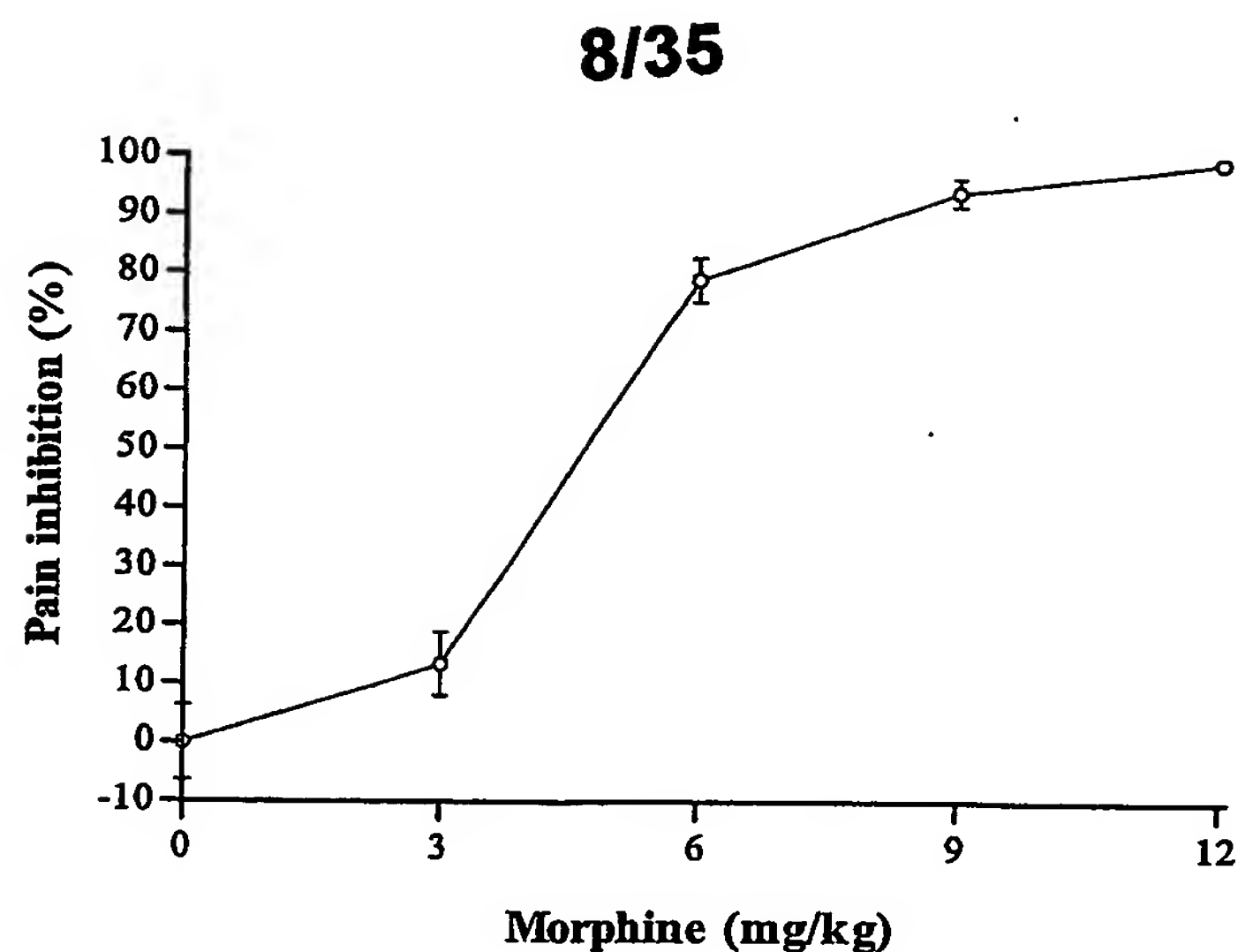


Barringtonside C = 3-O- $\alpha$ -L-arabinopyranosyl(1 $\rightarrow$ 3)-[ $\beta$ -D-galactopyranosyl(1 $\rightarrow$ 2)]- $\beta$ -D-glucuronopyranosyl  
barringtonenol C

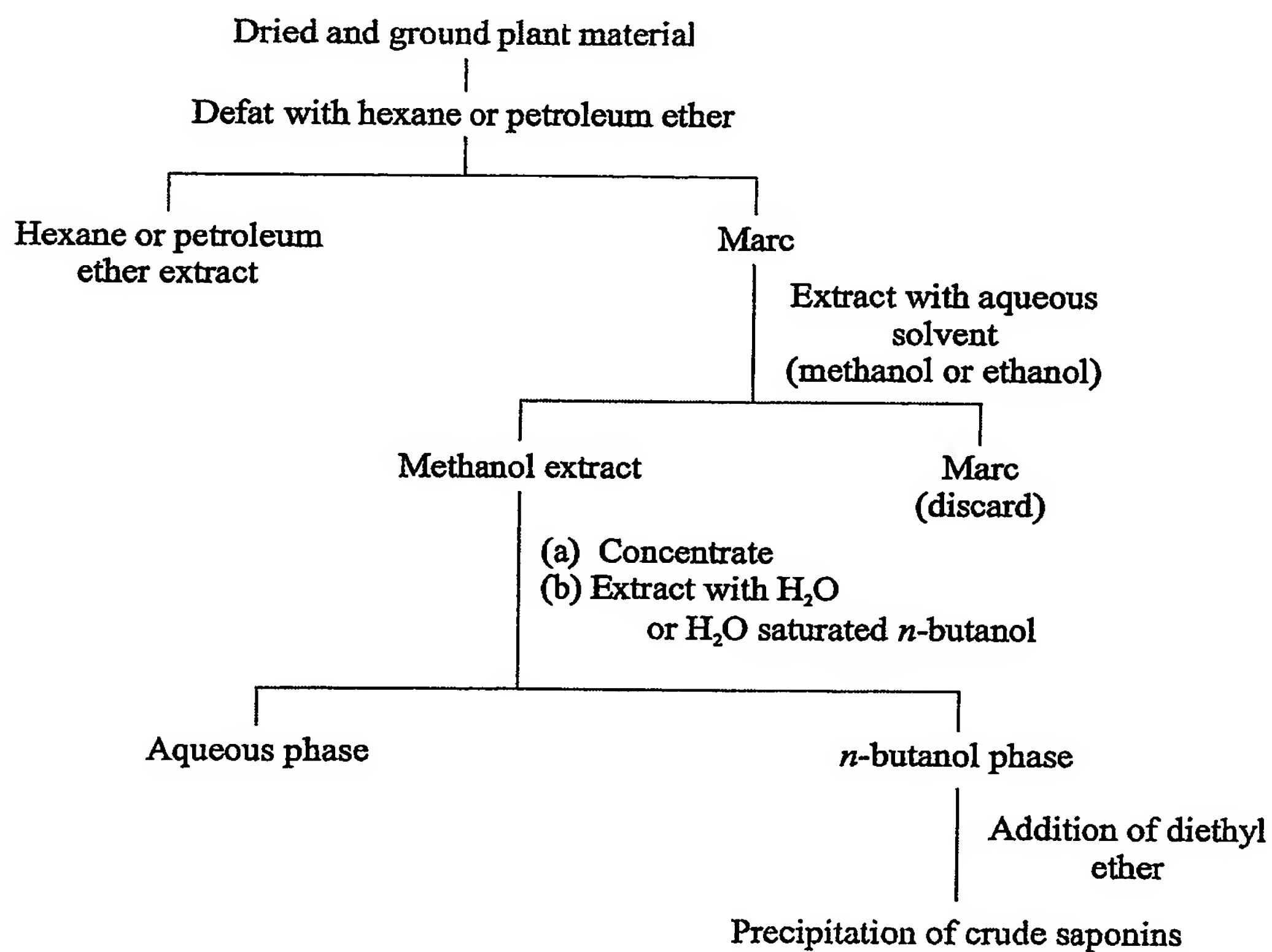
FIG 11

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**FIG 12** - Normal grooming response ( $\bar{x} \pm \text{S.E.}$ ;  $n = 6$ ).**FIG 13** - Control values ( $\bar{x} \pm \text{S.E.}$ ;  $n = 18$ ).



**FIG 14** - Dose response curve for morphine ( $\bar{x} \pm \text{S.E.}$ ;  $n = 6(\text{min})$ ).



**FIG 15** - Schematic for the preparation of crude saponin mixtures.



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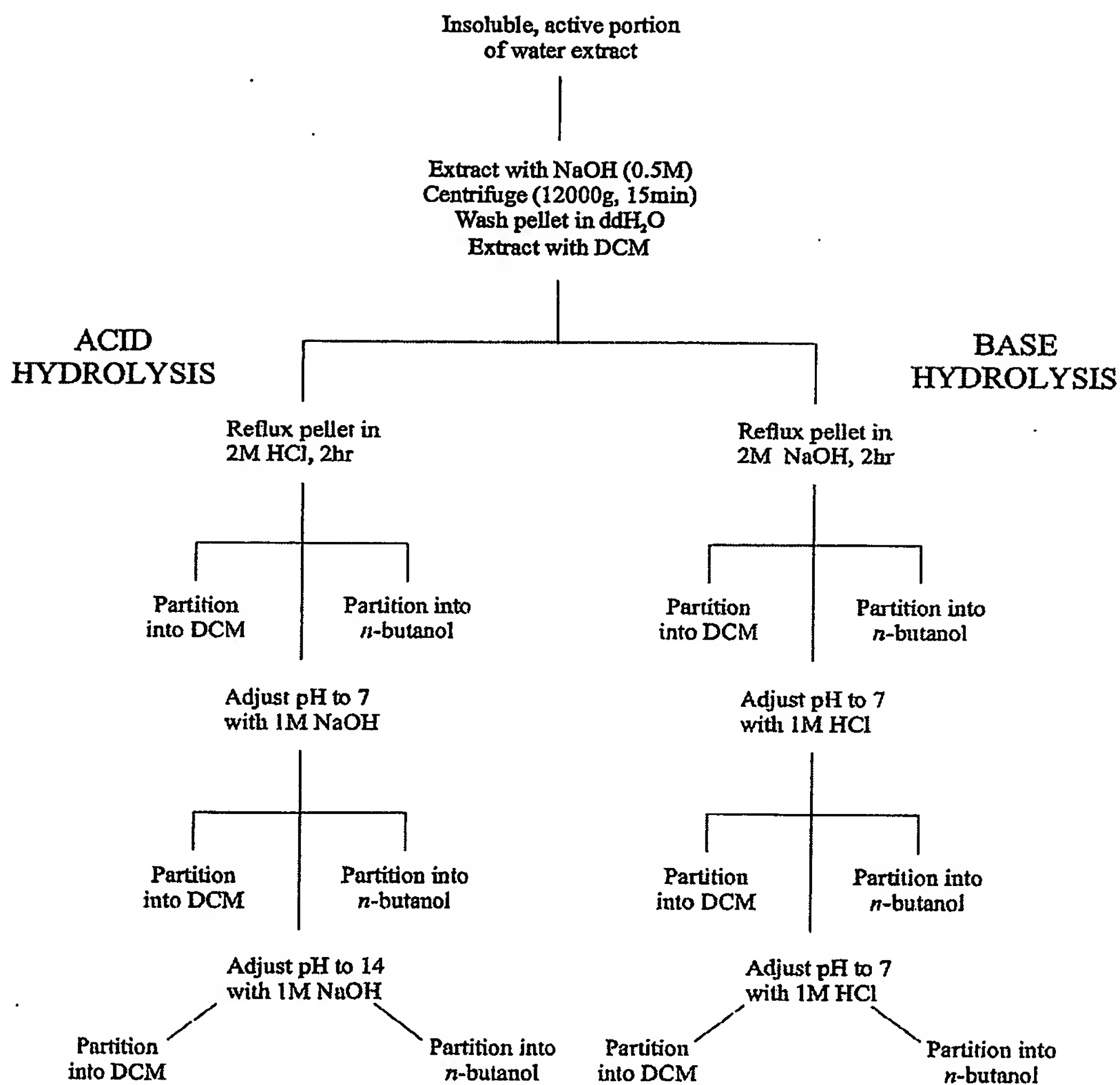
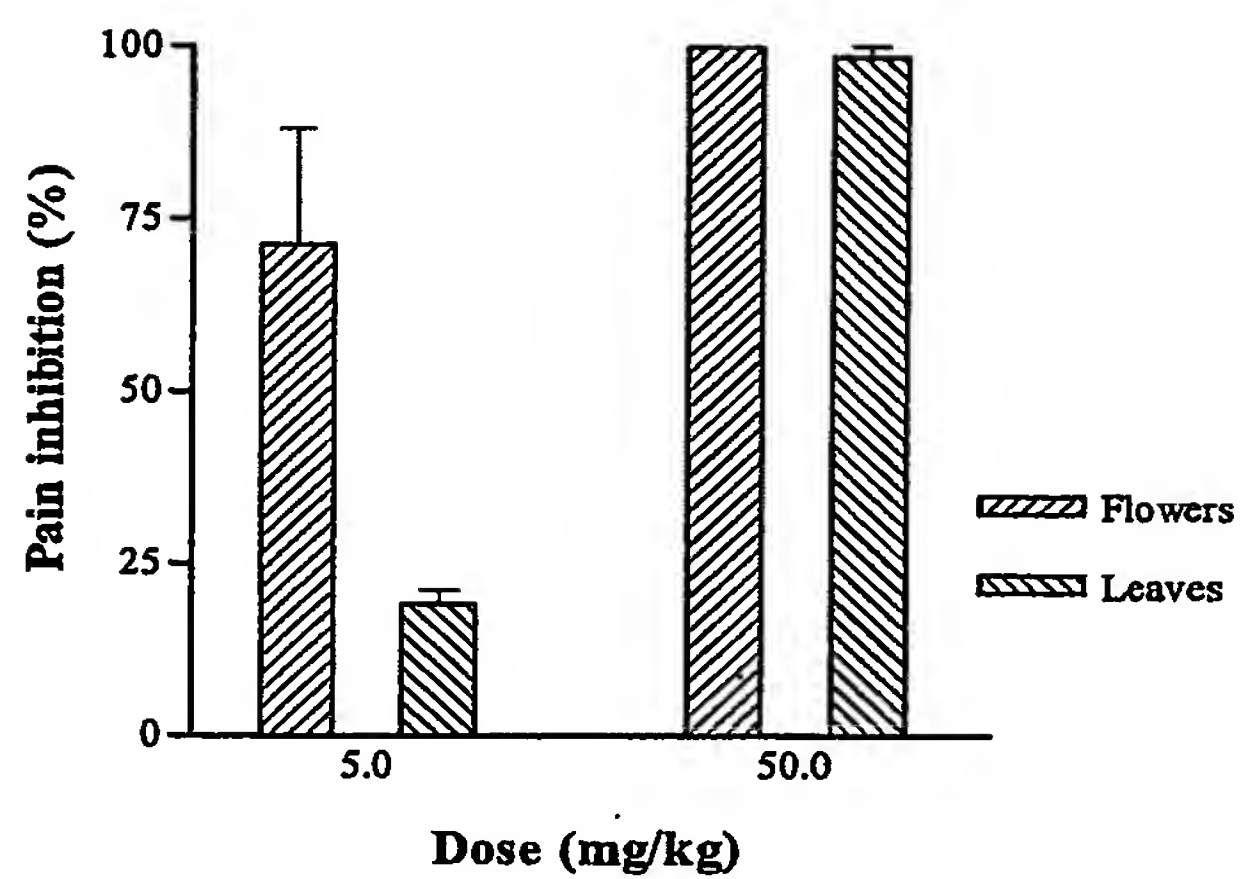
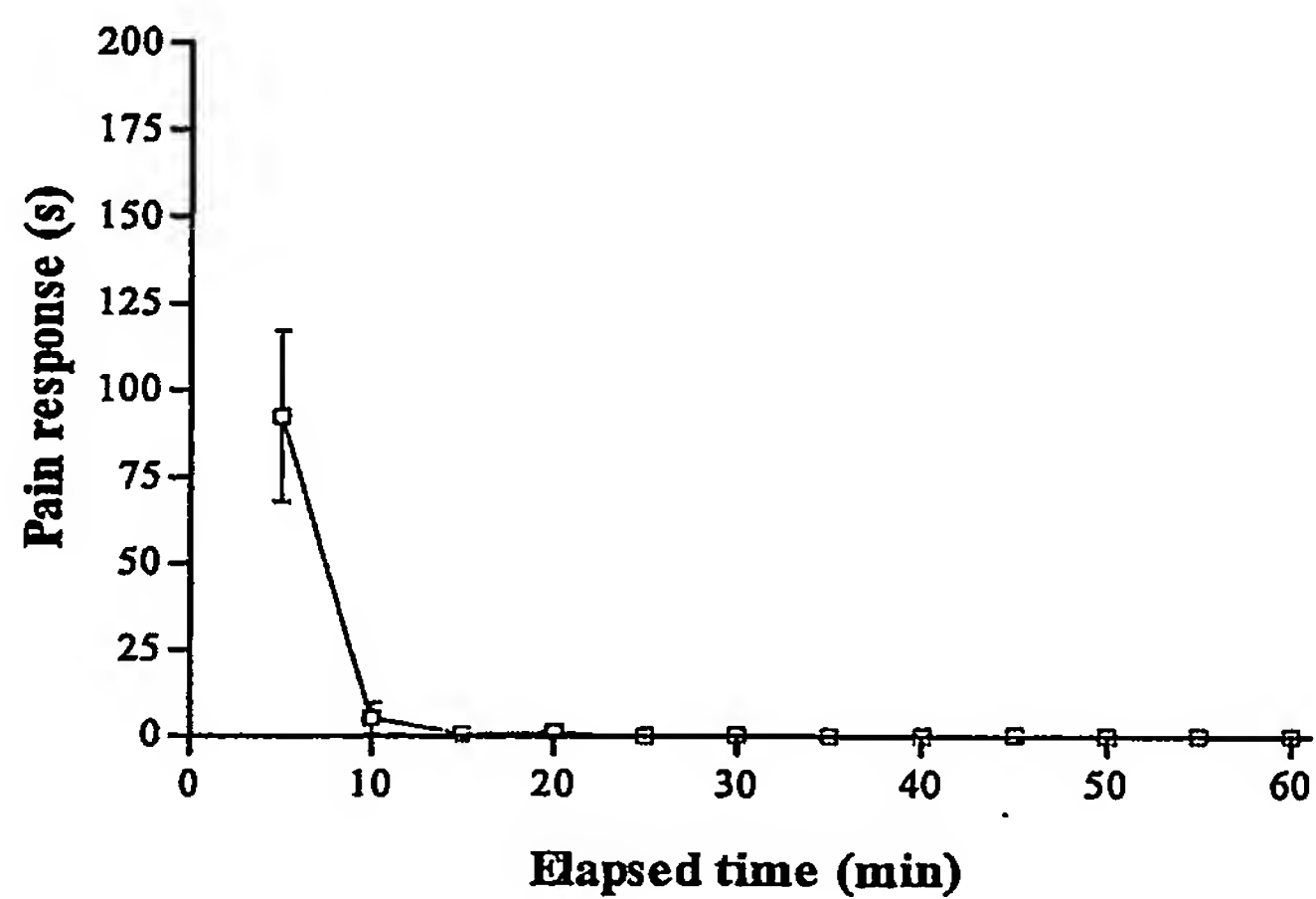


FIG 16 - Acid and base hydrolysis scheme.

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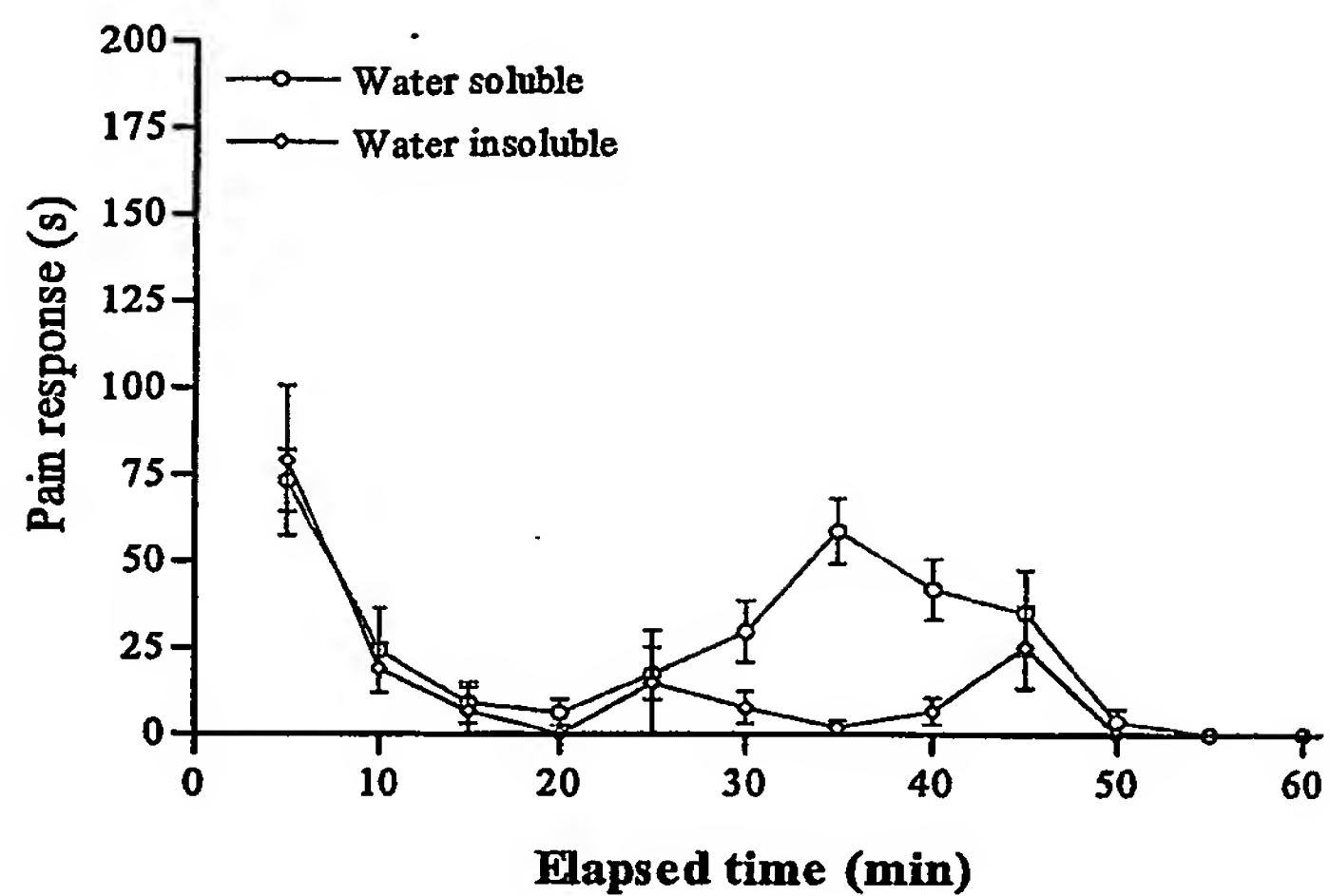


**FIG 17 -** Analgesic activity of water extract of flowers and leaves of *B. acutangula* ( $\bar{x} \pm \text{SE}$ ,  $n=2$ ).

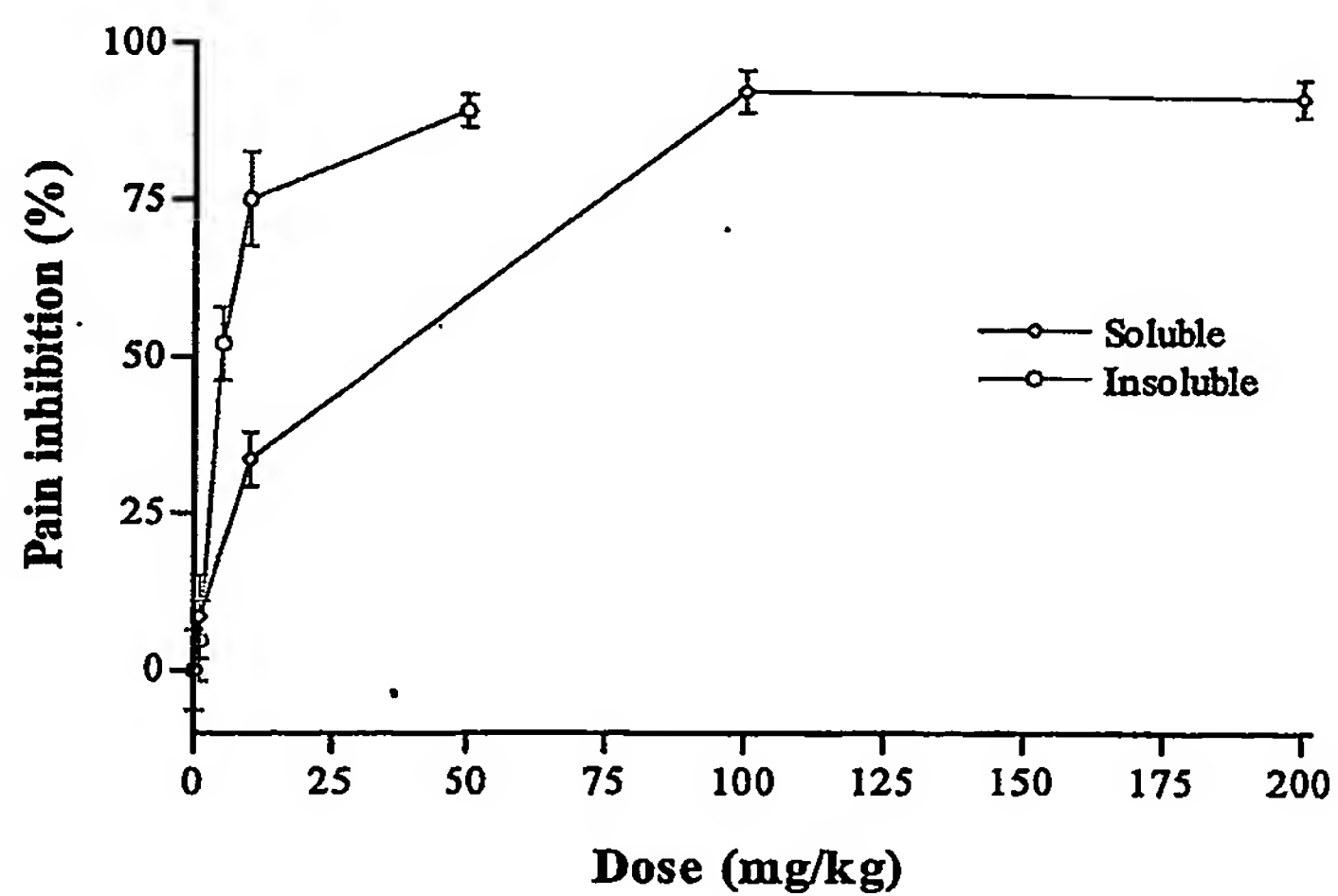


**FIG 18 -** Analgesic activity of crude water extract ( $\bar{x} \pm \text{SE}$ ,  $n=5$ ).

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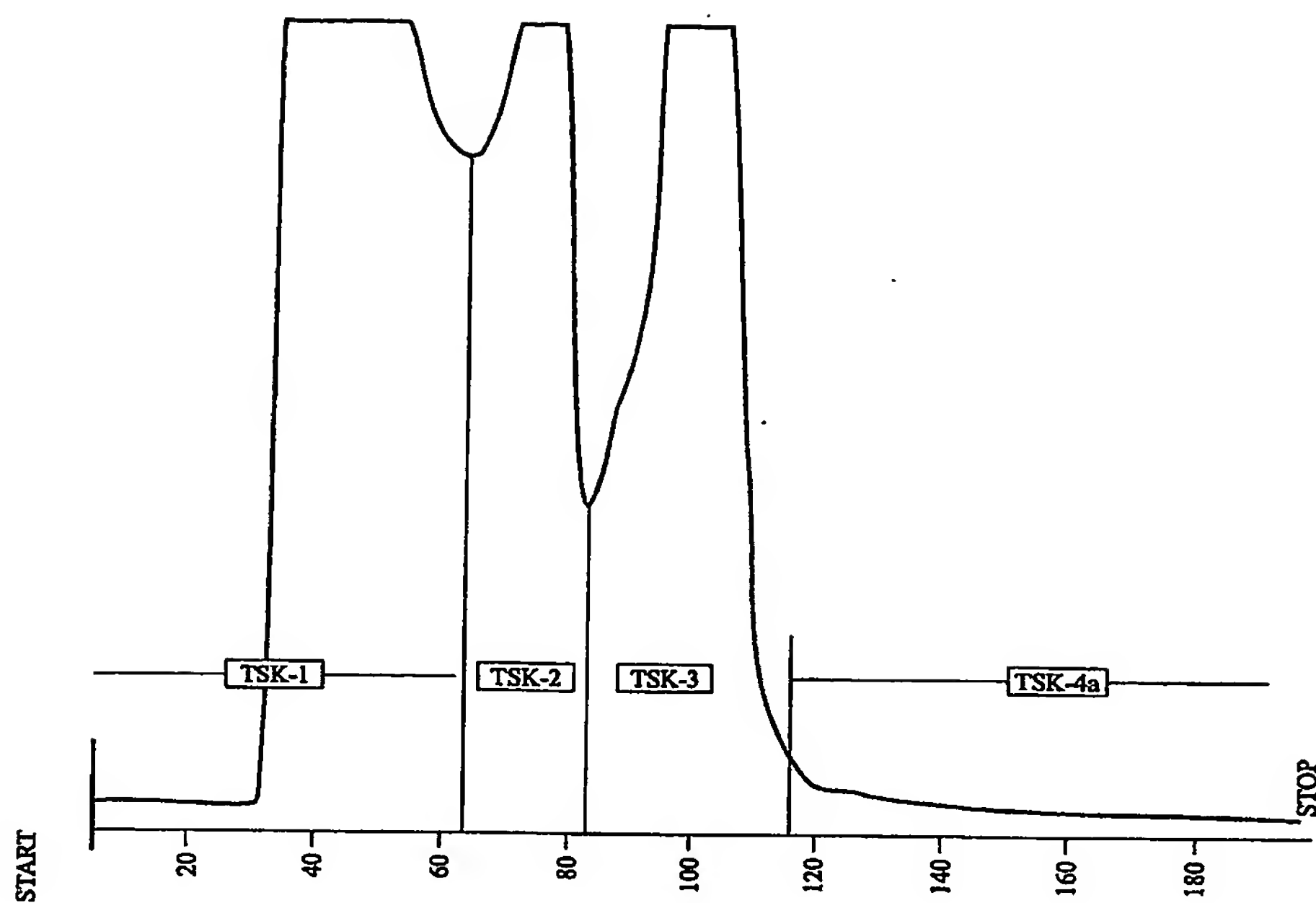
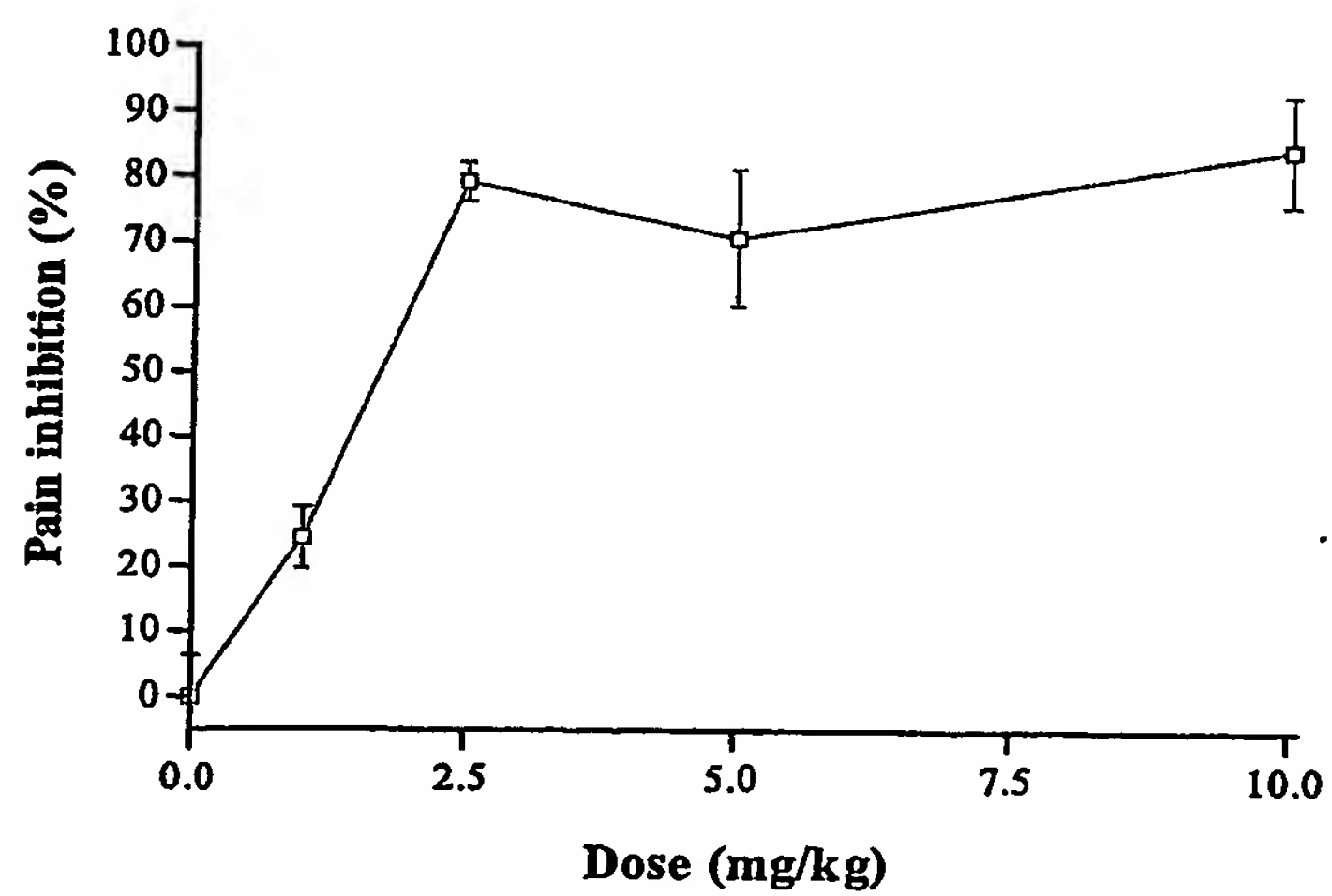


**FIG 19** - Analgesic activity of crude water soluble (n=9) and insoluble (n=4) portions of the water extract ( $\bar{x} \pm SE$ ).



**FIG 20** - Dose response curves for water extract ( $\bar{x} \pm SE$ , n=4).

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**FIG 21 - Preparative gel permeation column.****FIG 22 - Dose response curve for TSK-4a ( $\bar{x} \pm SE$ , n=3).**

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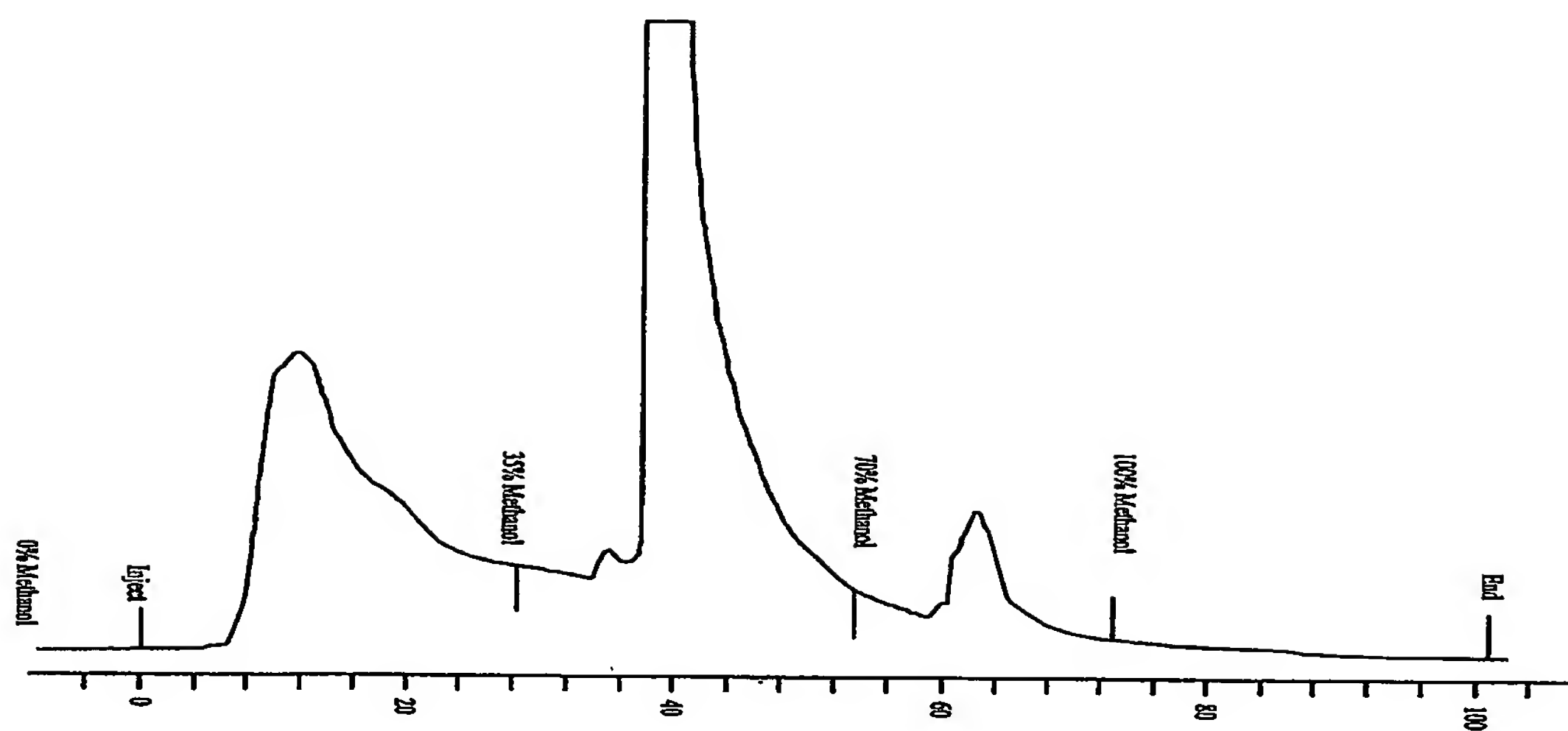


FIG 23 - C18 separation of TSK-4a.

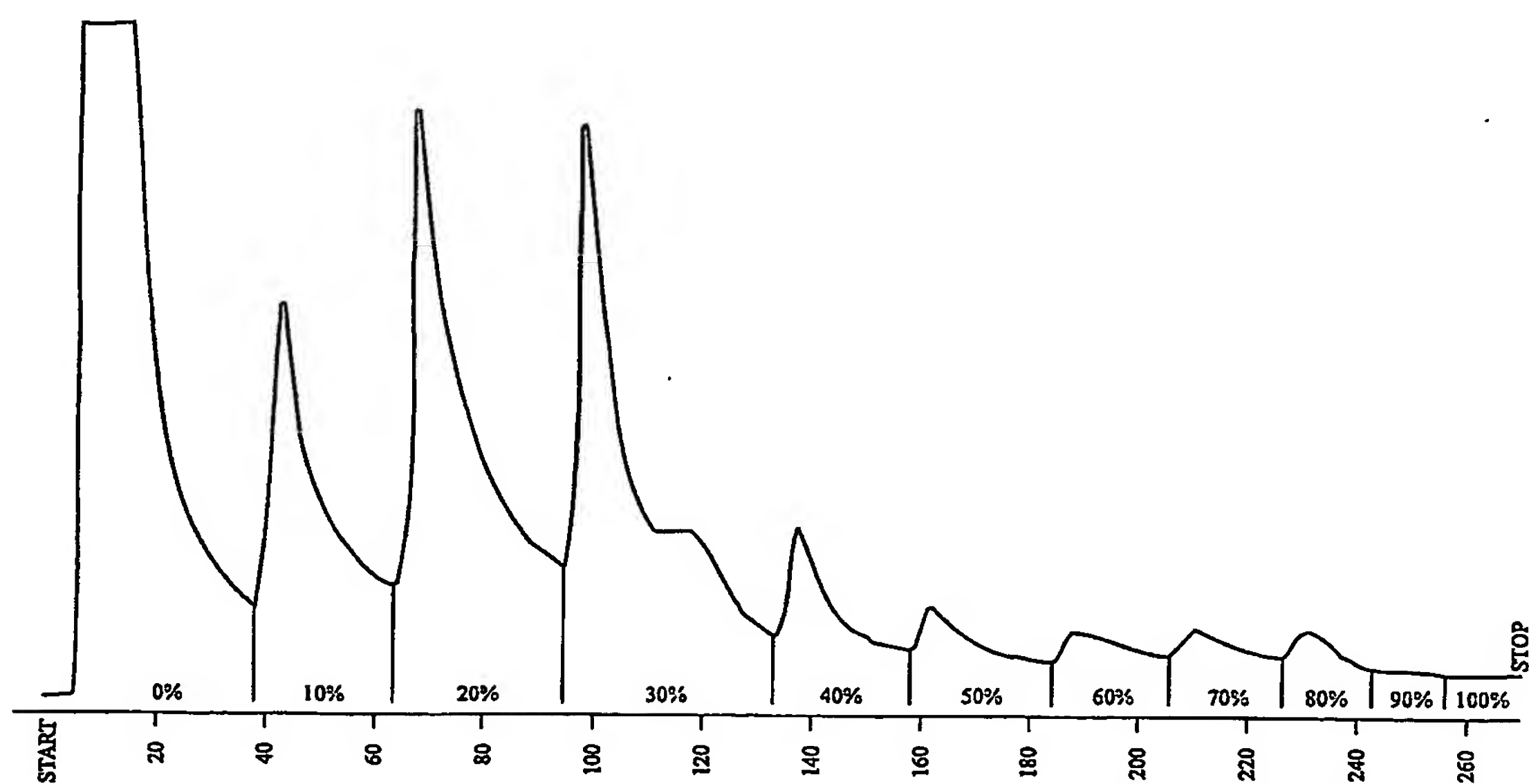


FIG 24 - C18 preparative separation of TSK-4a.

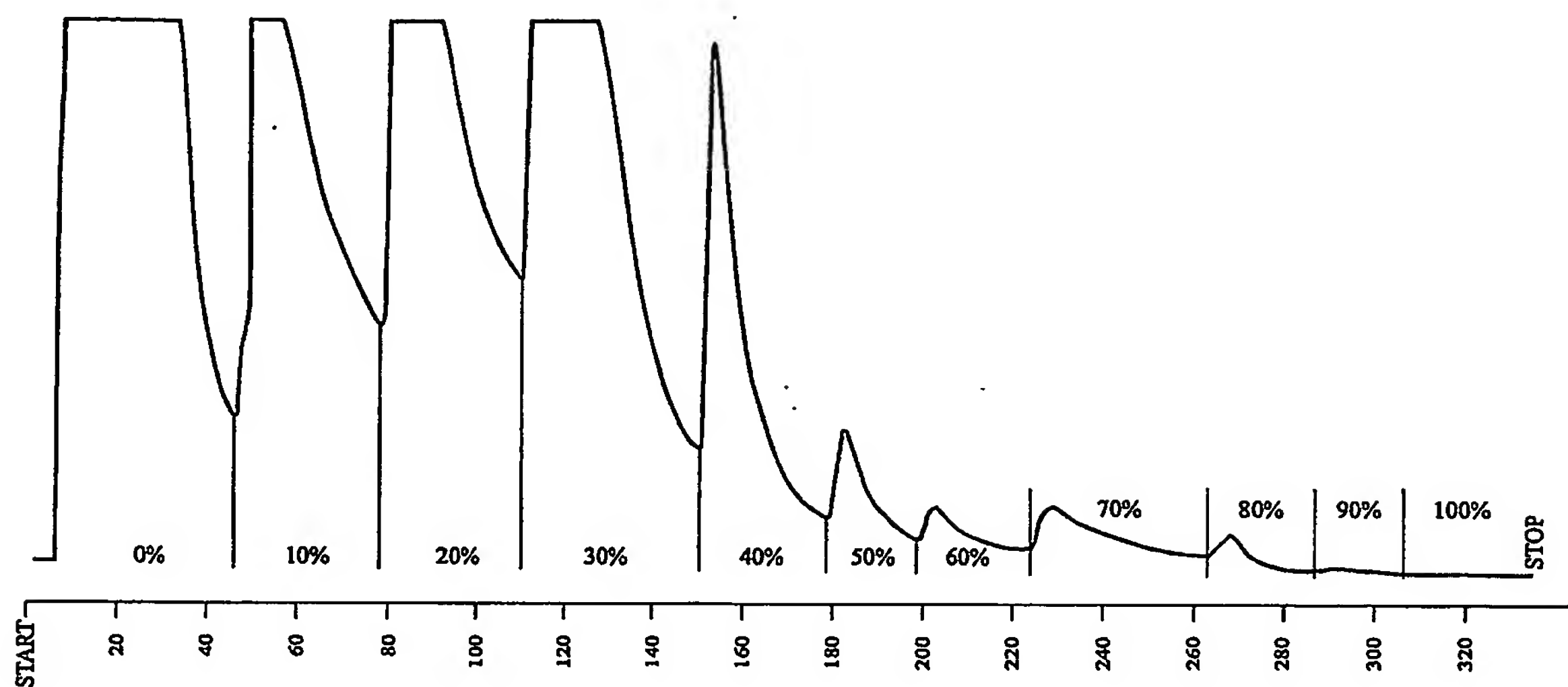


FIG 25 - Preparative C18 chromatogram of H<sub>2</sub>O extract

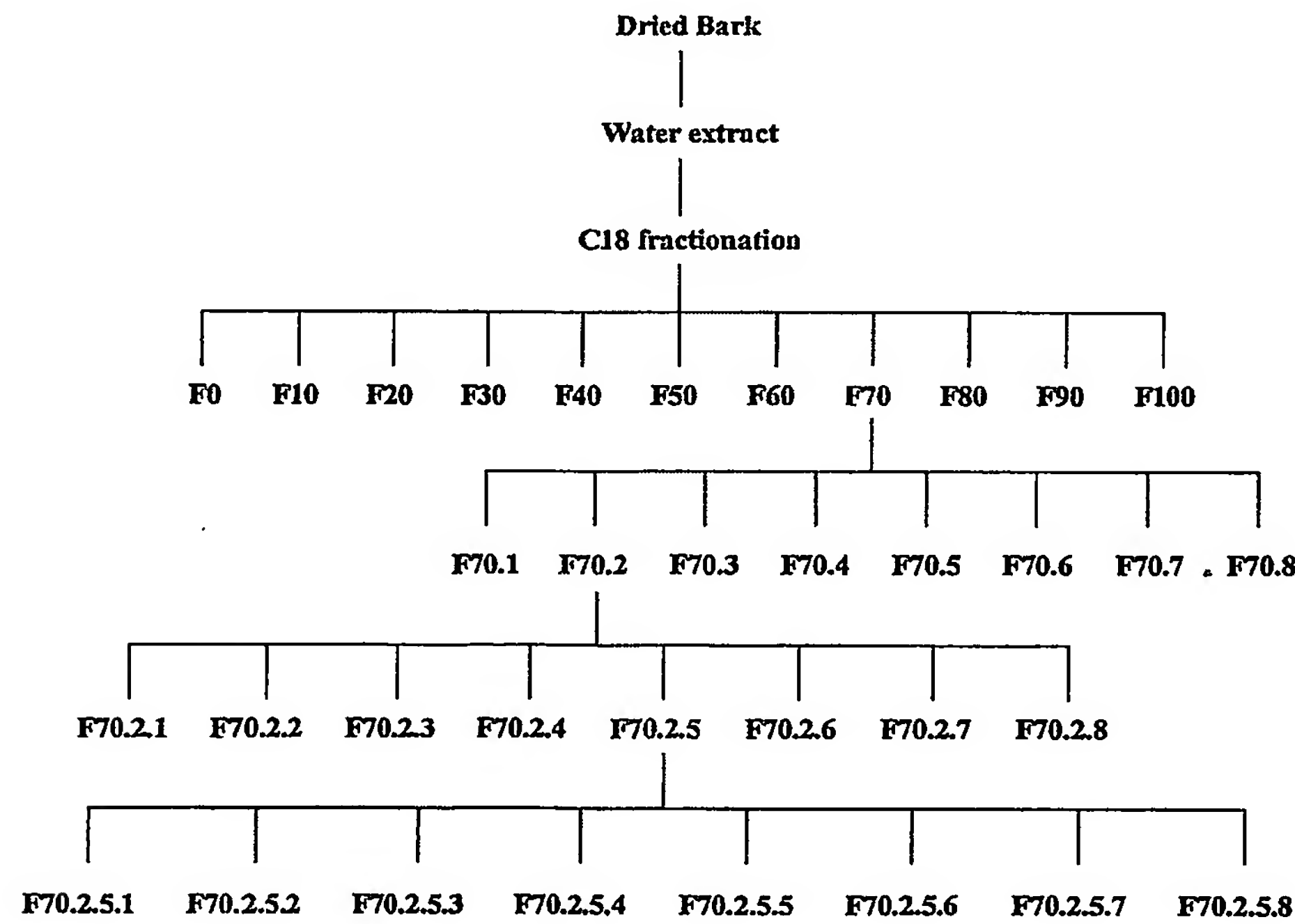


FIG 26 - Outline of numbering system compound F70.2.5.2.

Analytical separations

Preparatory separations

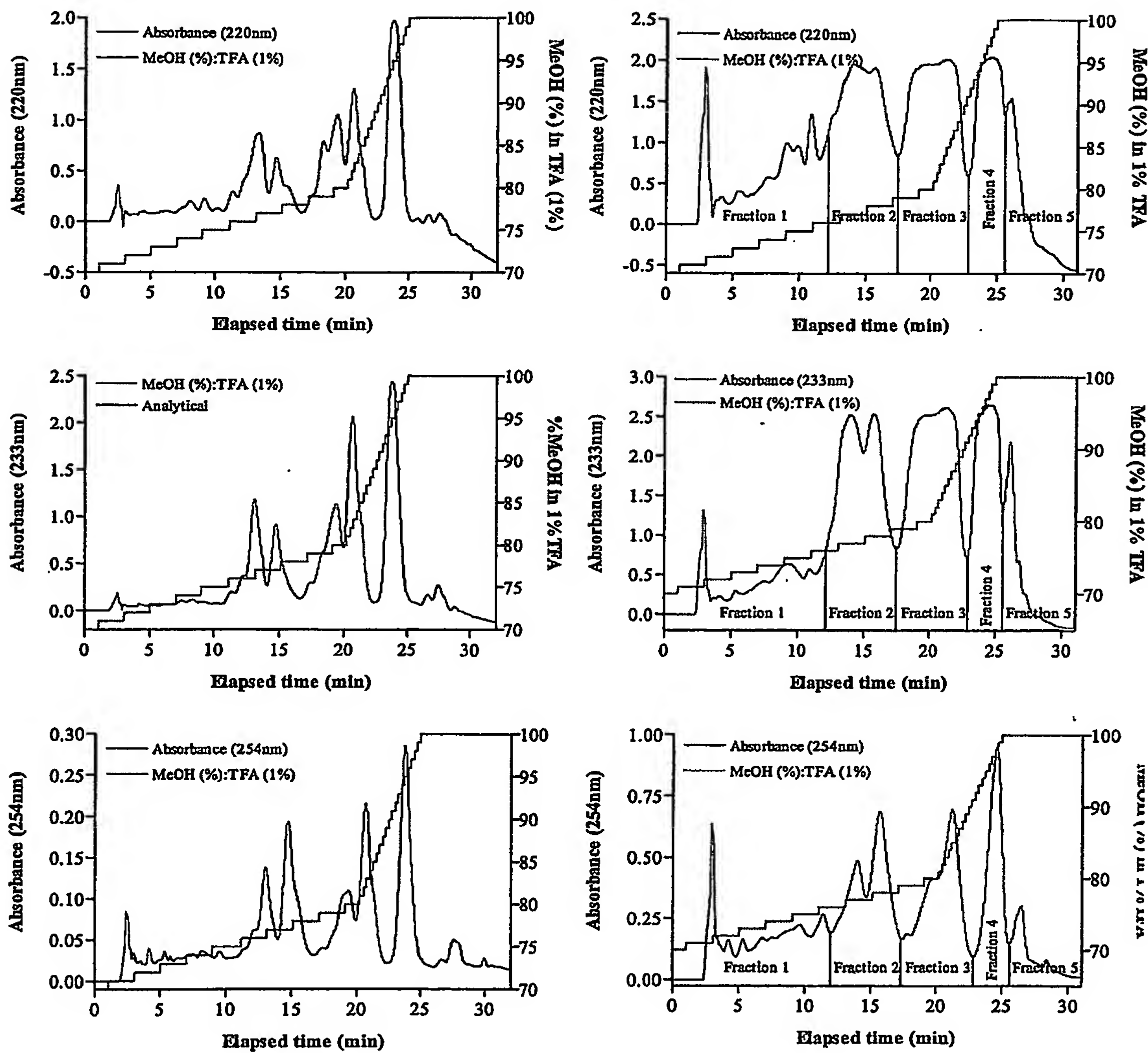
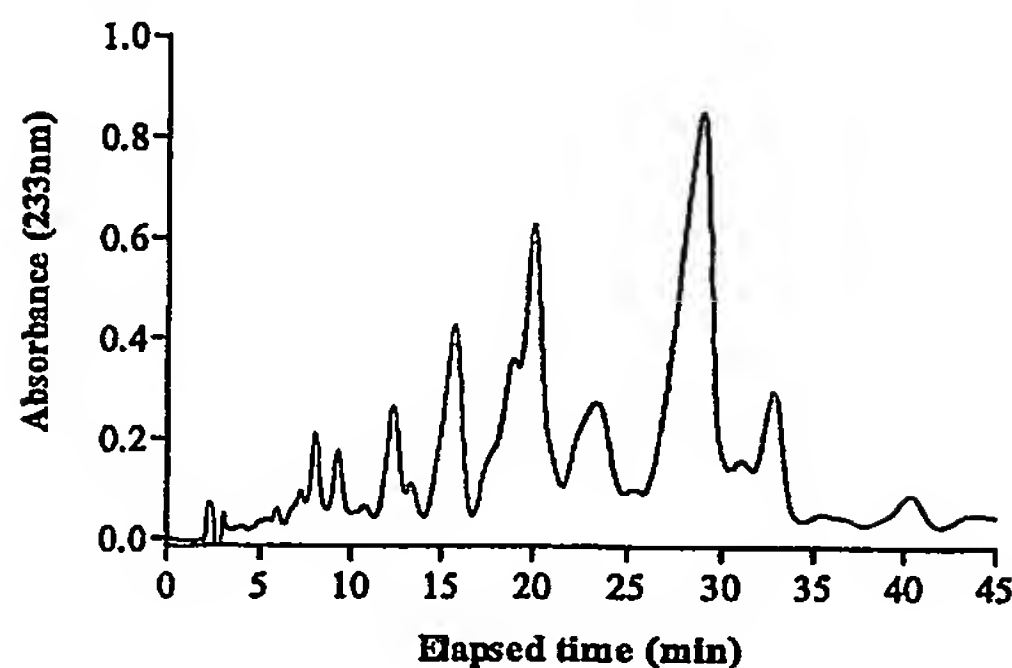


FIG 27 - Separation of fraction eluting at 70% MeOH (F70).

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## Analytical separations



## Preparatory separations

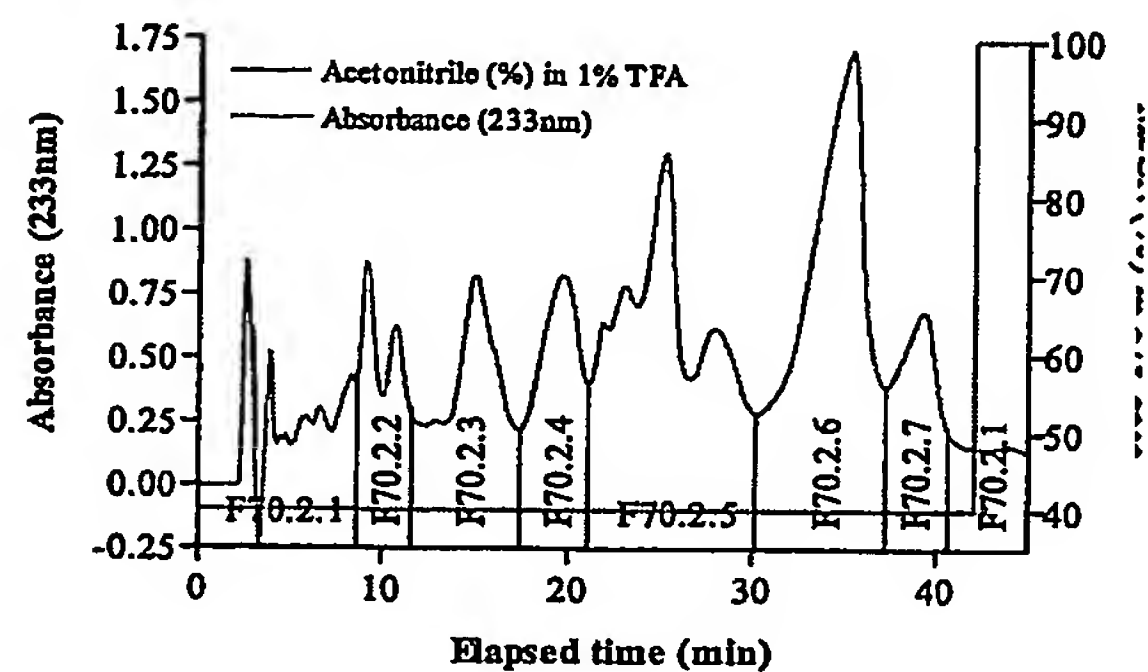


FIG 28 - Separation of fraction F70.2 (40%MeCN in 1%TFA).

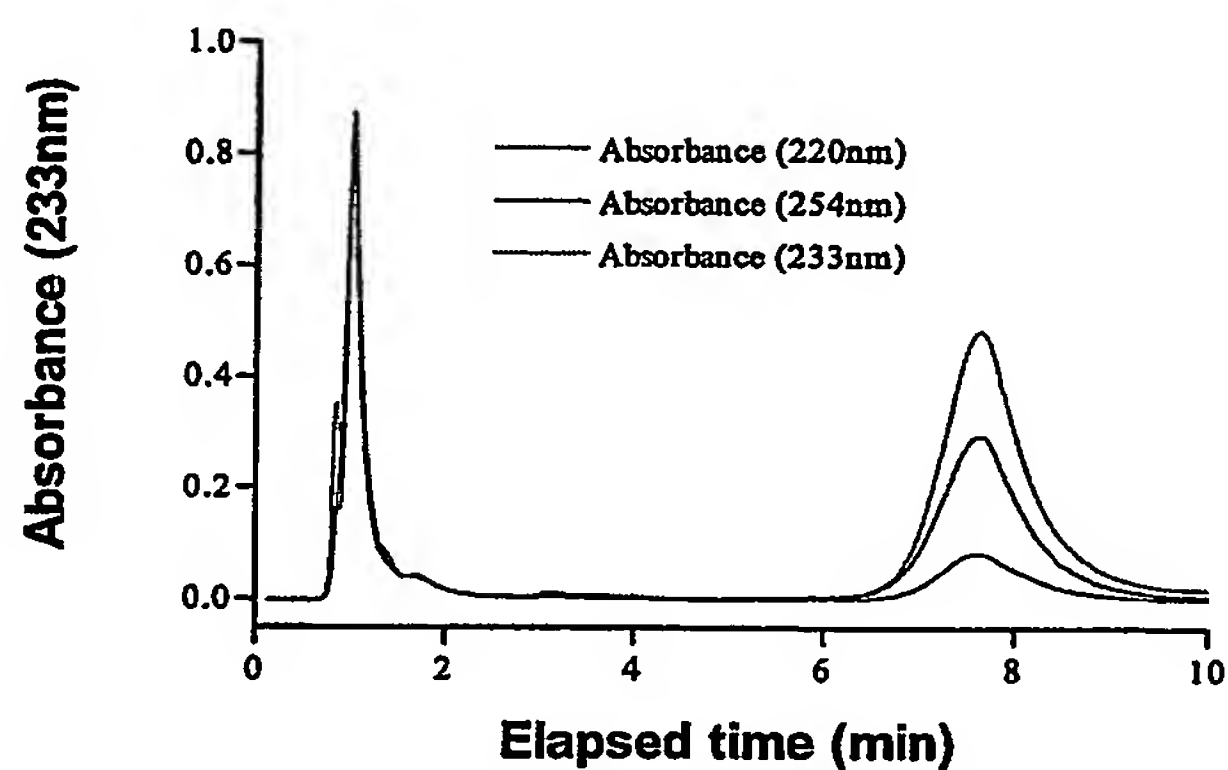


FIG 29 - Chromatogram of F70.2.6.

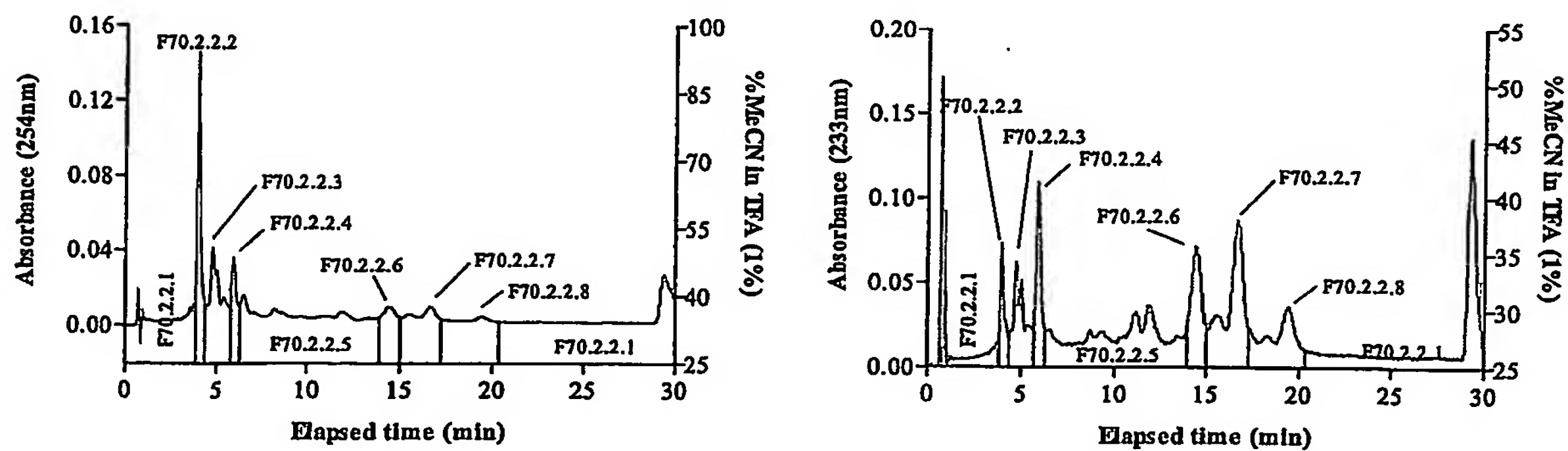


FIG 30 - Separation of fraction F70.2.2 at 254nm (left) and 233nm (right).



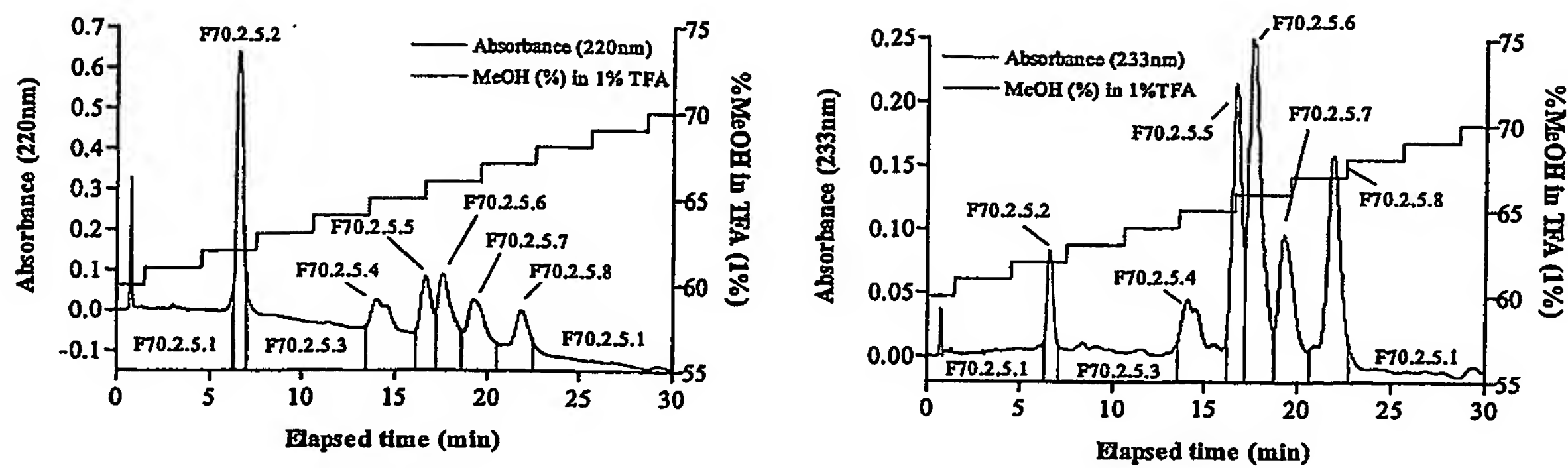
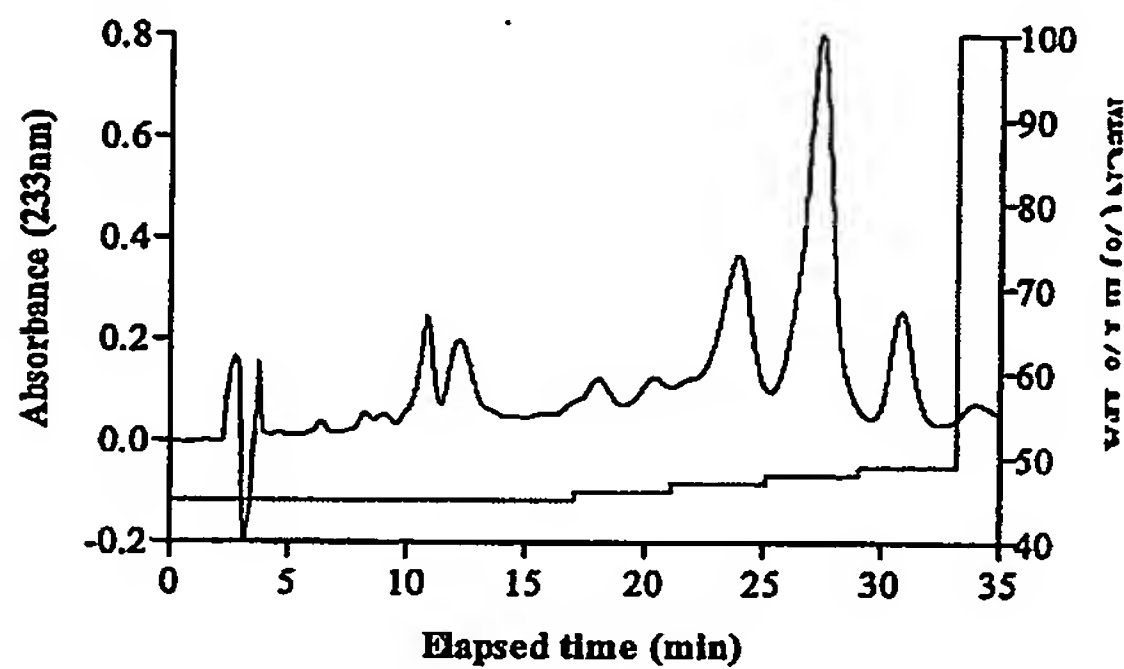


FIG 31 - Separation of fraction F70.2.5 at 220nm (left) and 233nm (right).

Analytical separations



Preparatory separations

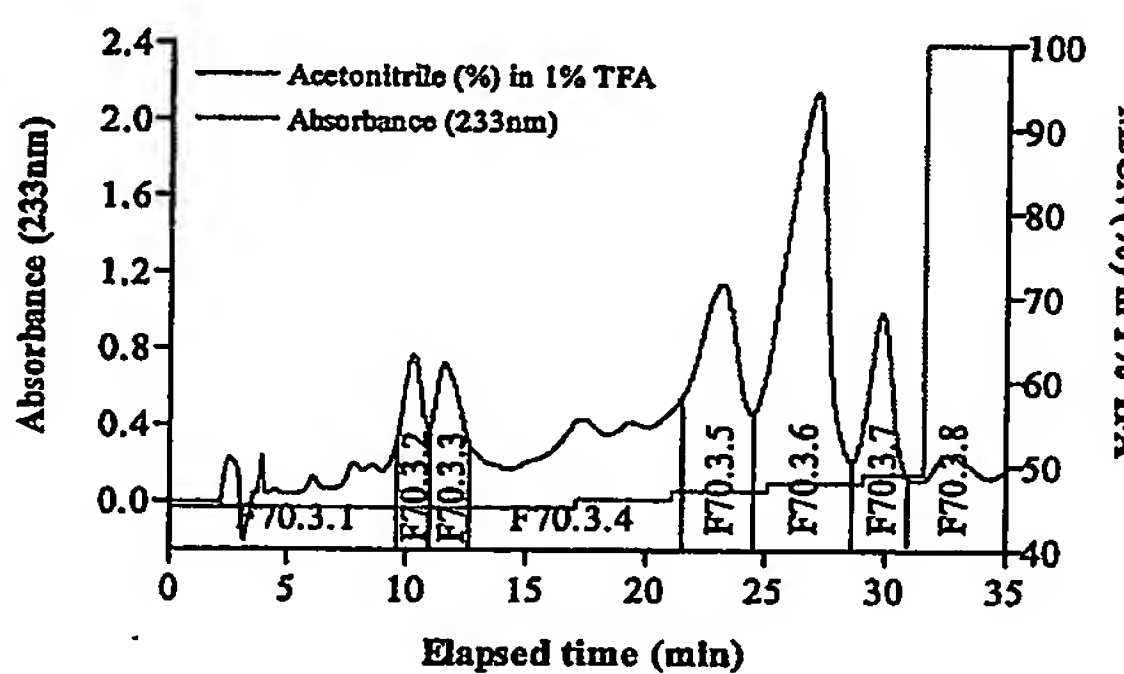
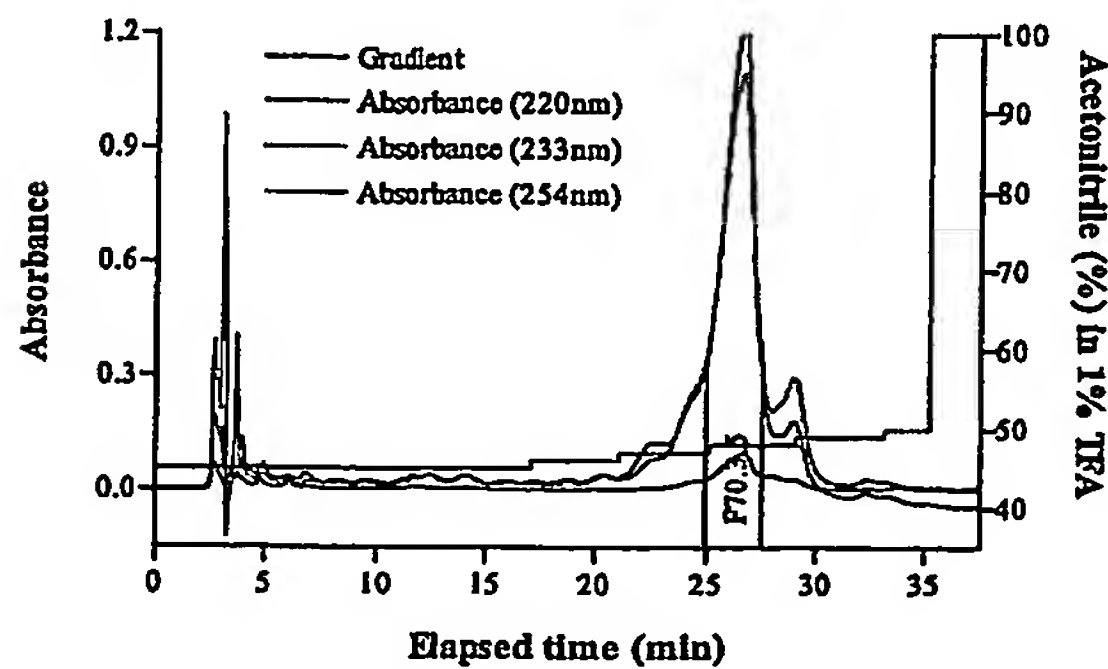


FIG 32 - Separation of fraction F70.3.

Fraction F70.3.5



Fraction F70.3.7

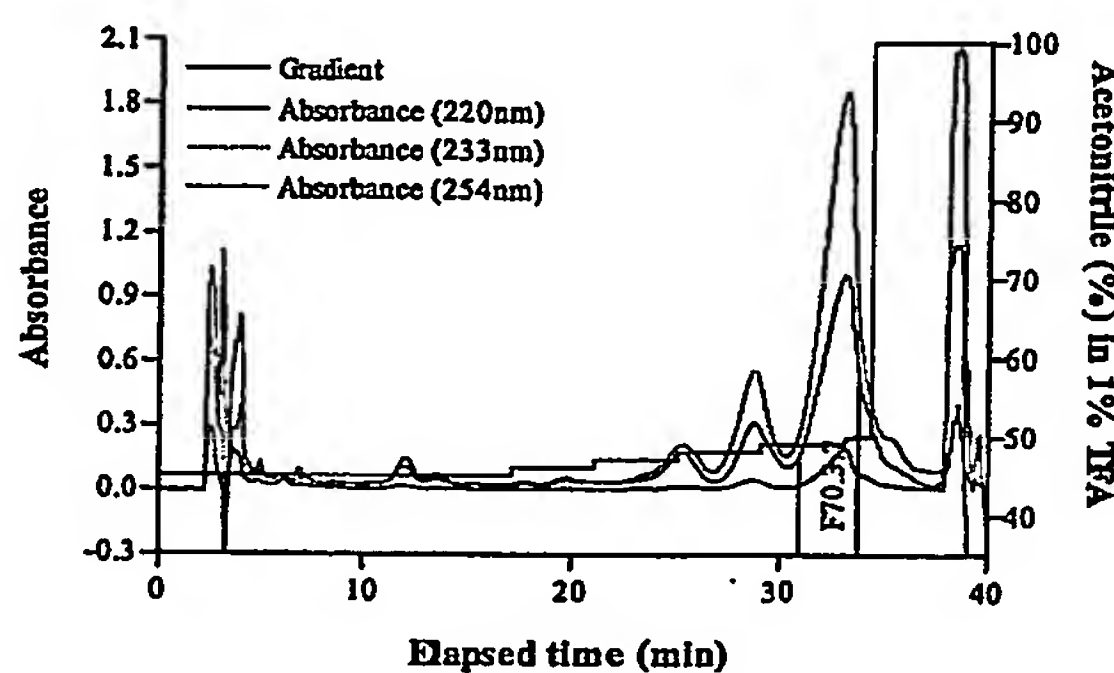


FIG 33 - Chromatograms of F70.3.5 and F70.3.7.

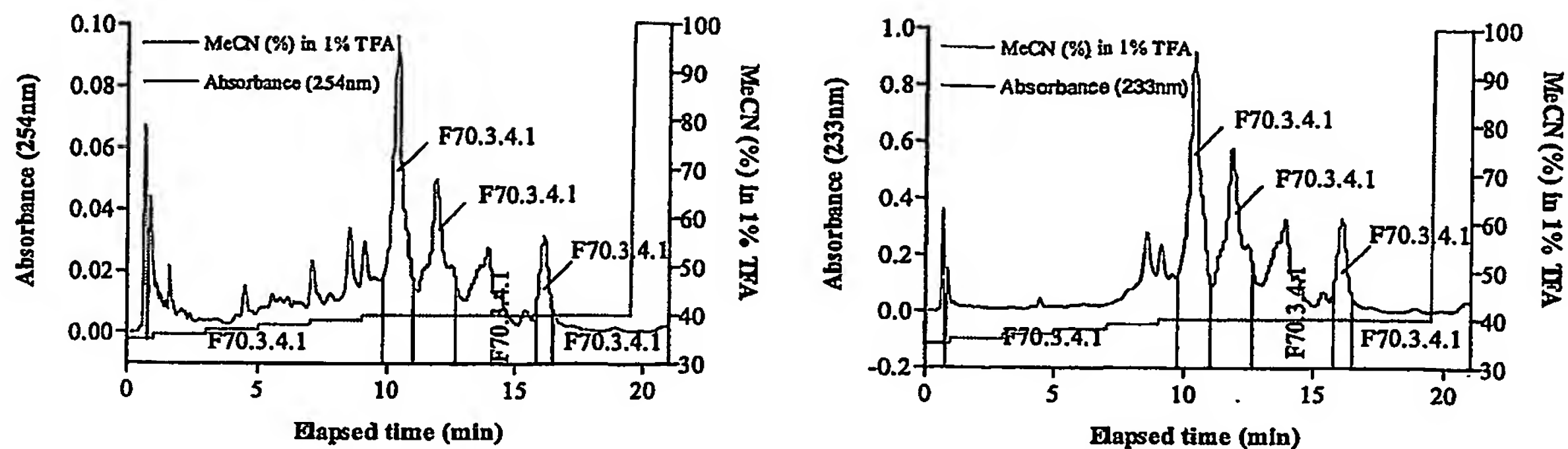
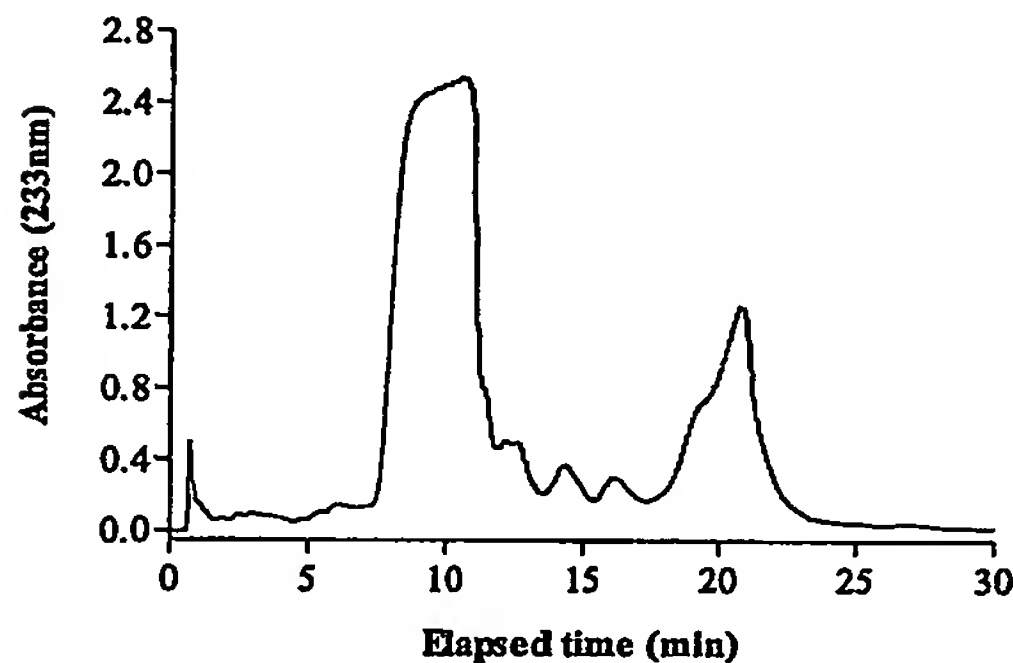


FIG 34 - Analytical separation of fraction F70.3.4 at 254 and 233nm.

Analytical separation



Preparative separation

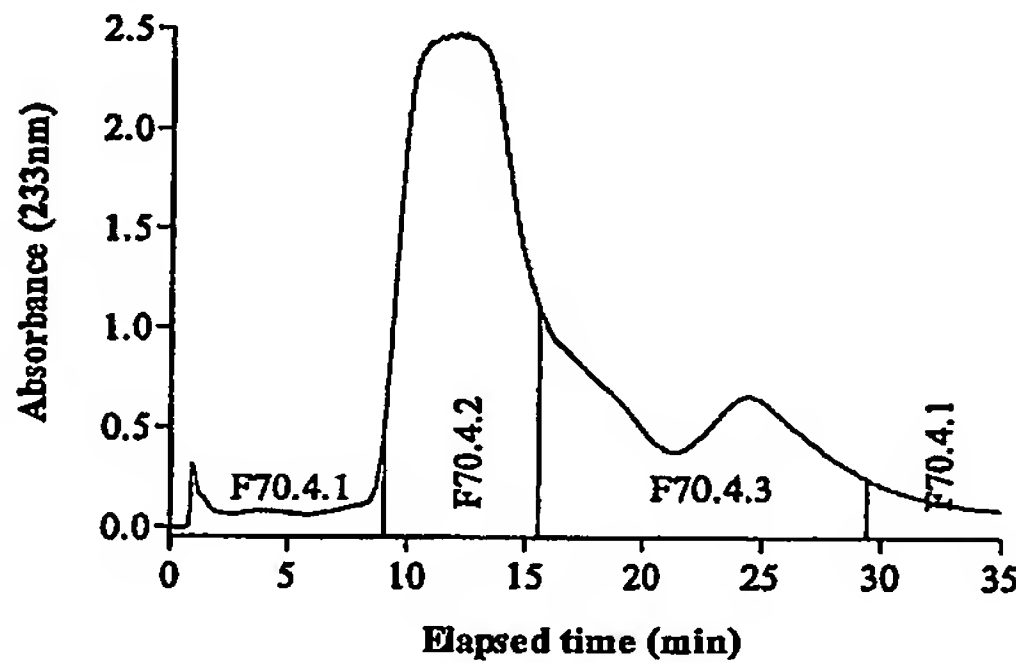


FIG 35 - Separation of F70.4.

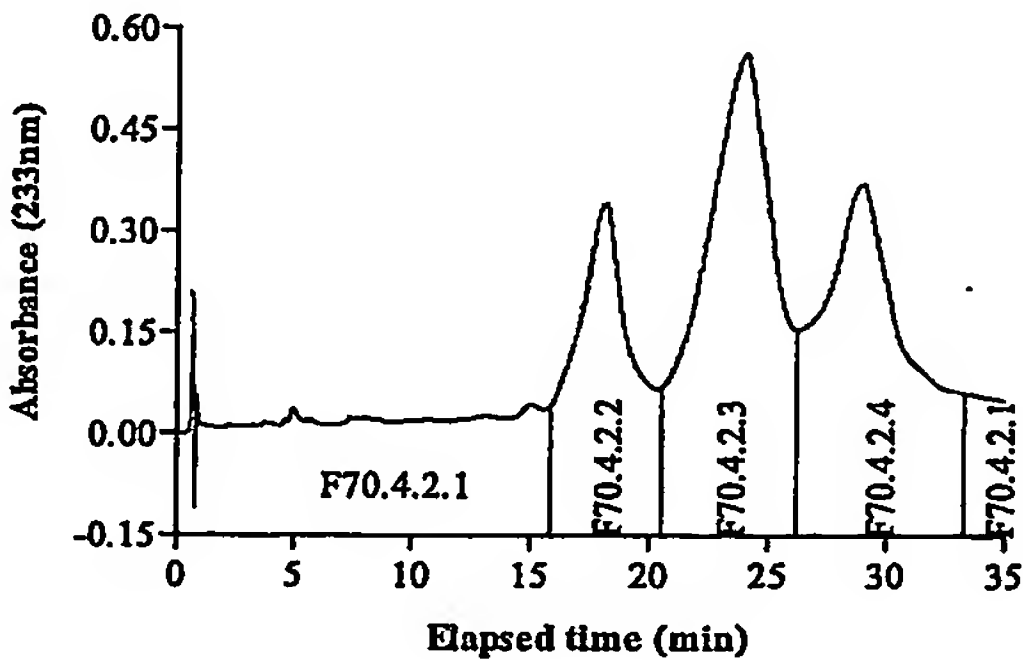
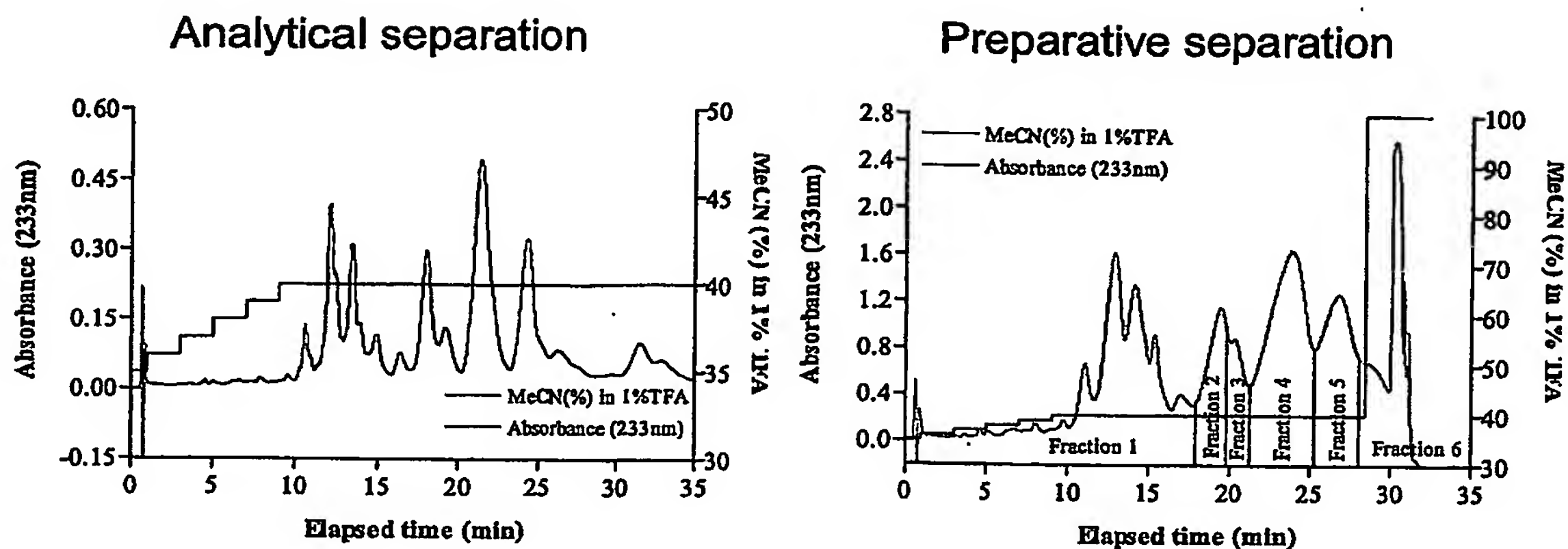
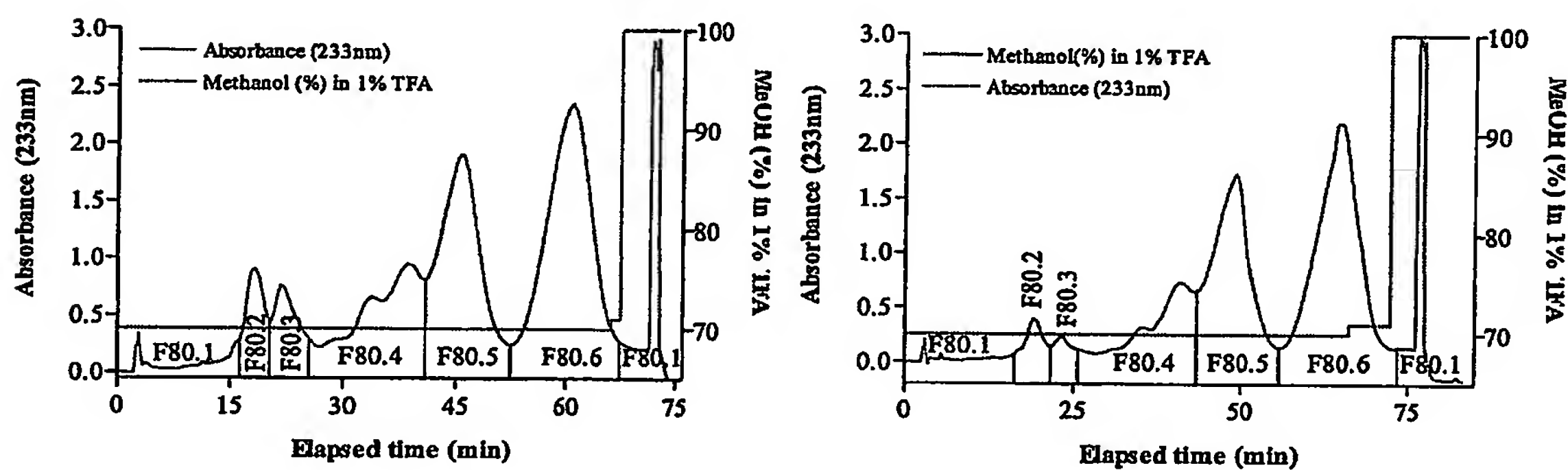


FIG 36 - Separation of F70.4.2.

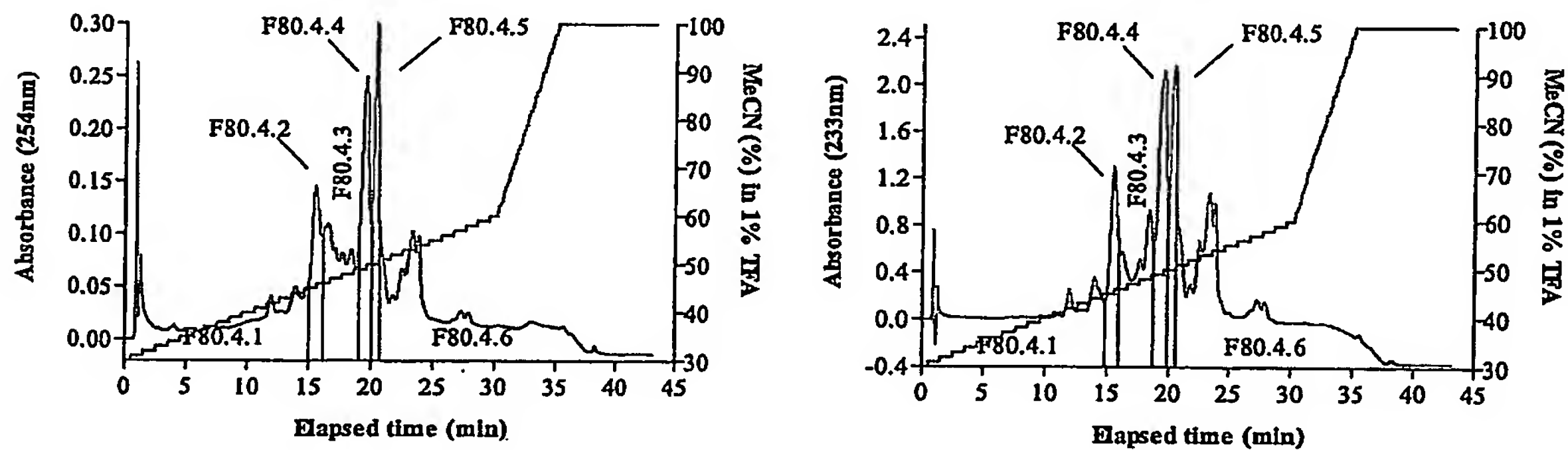
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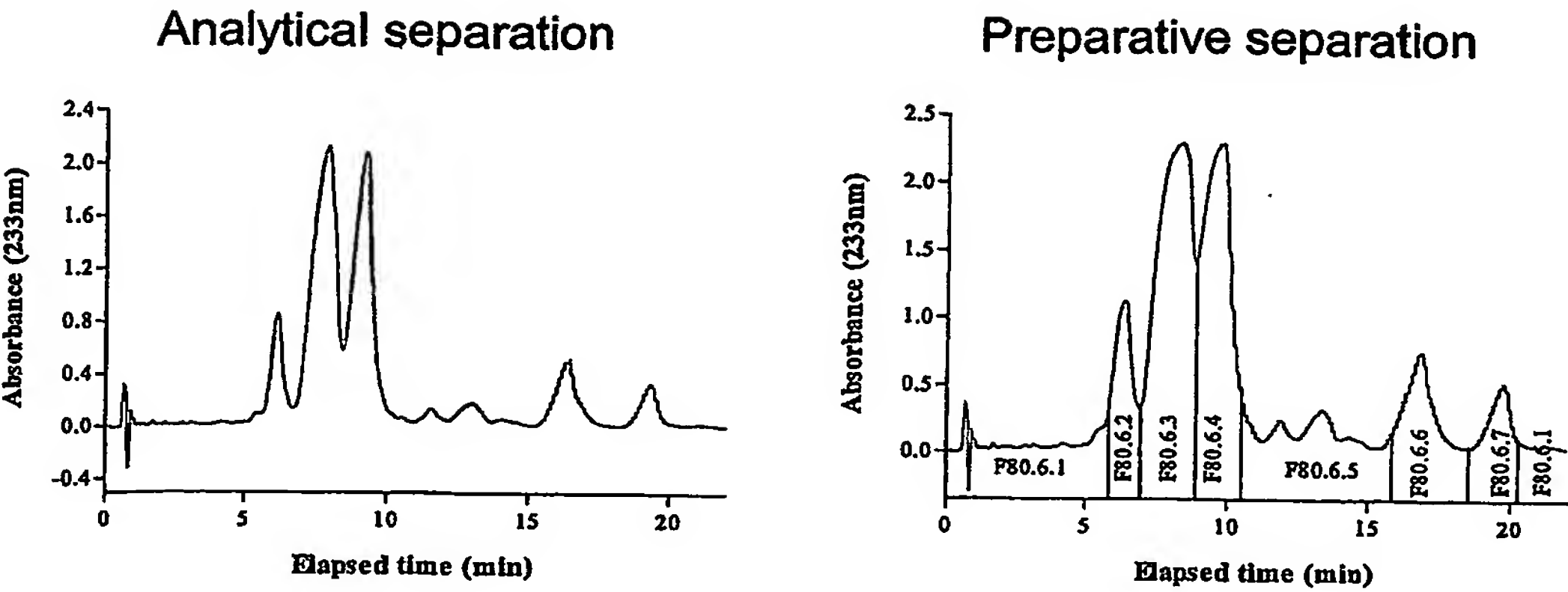
**FIG 37 – Analytical separation (left) and preparative separation (right) of F70.4.3.**



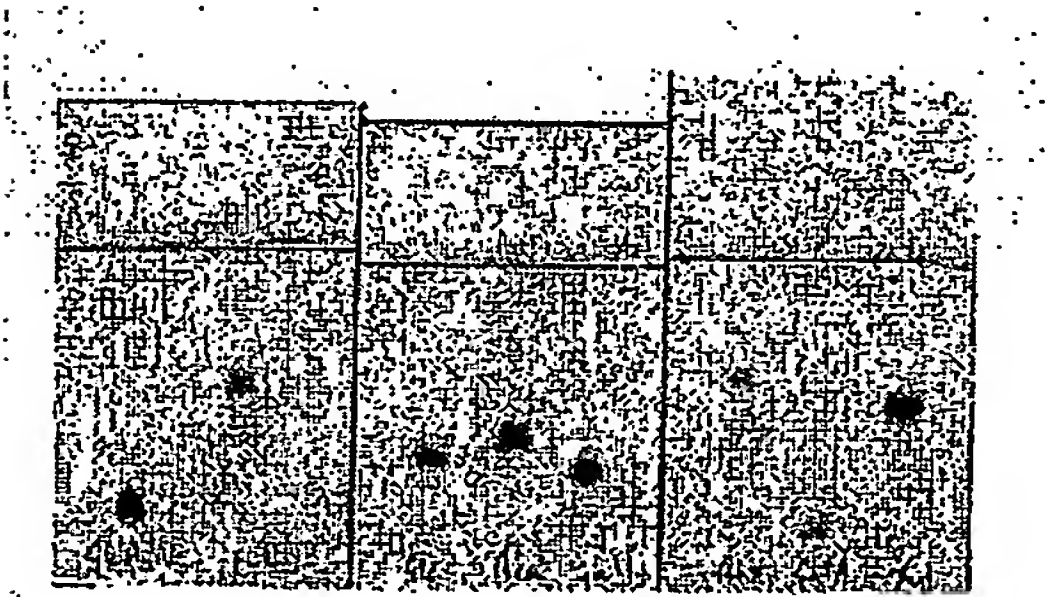
**FIG 38 - Preparative chromatograms showing loss of peaks F80.2 & F80.3.**



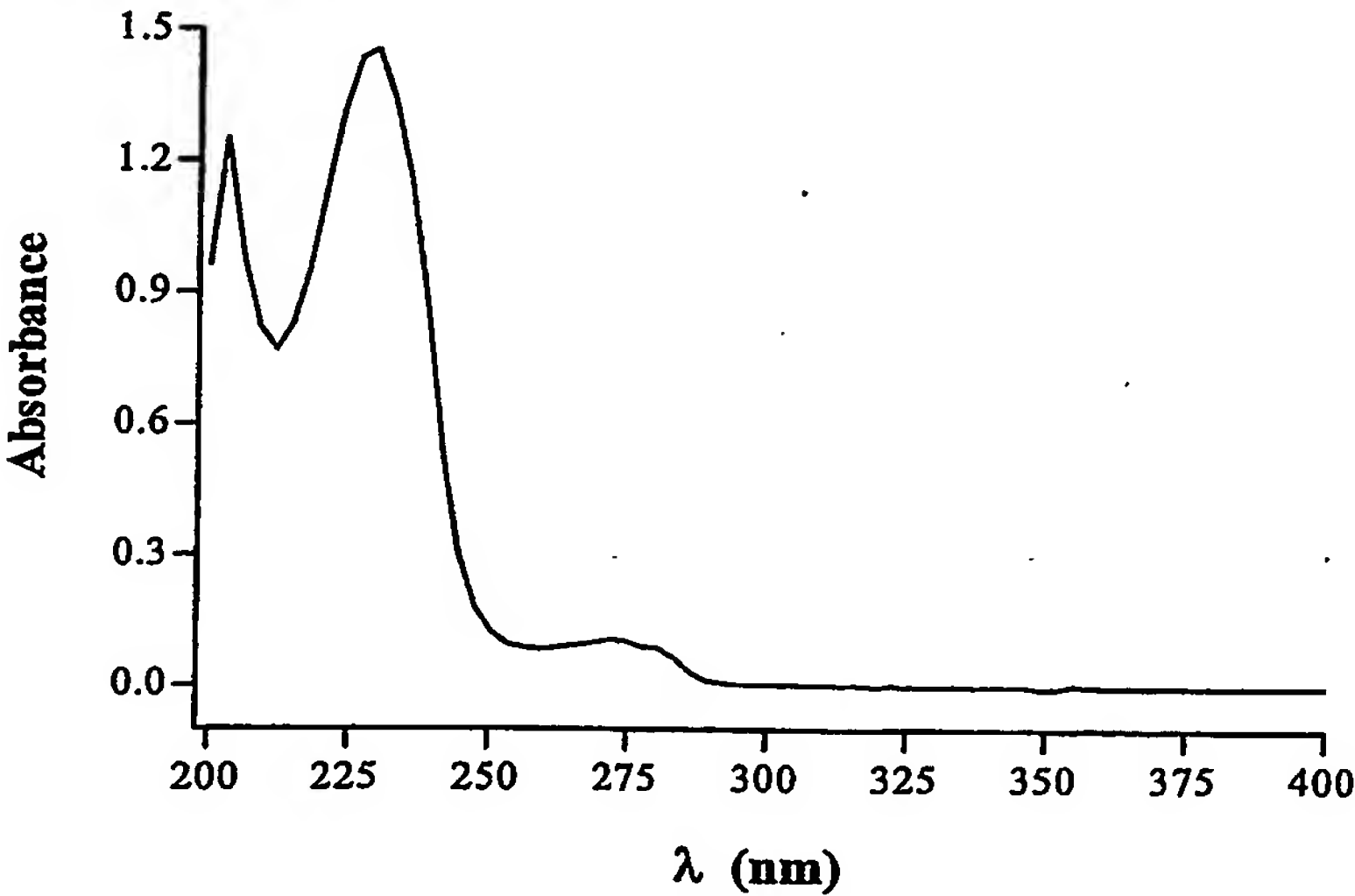
**FIG 39 - Preparative chromatograms of F80.4.**



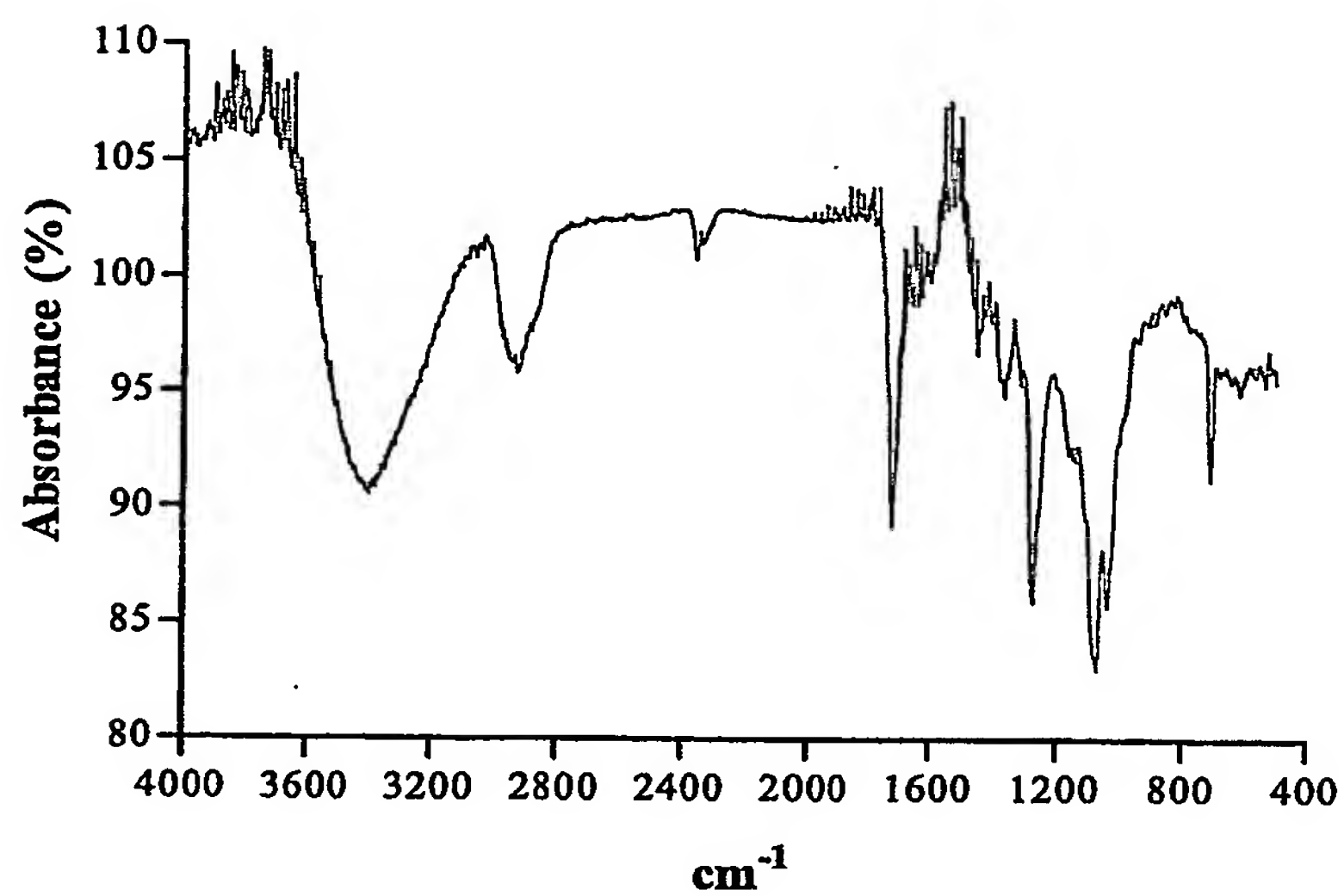
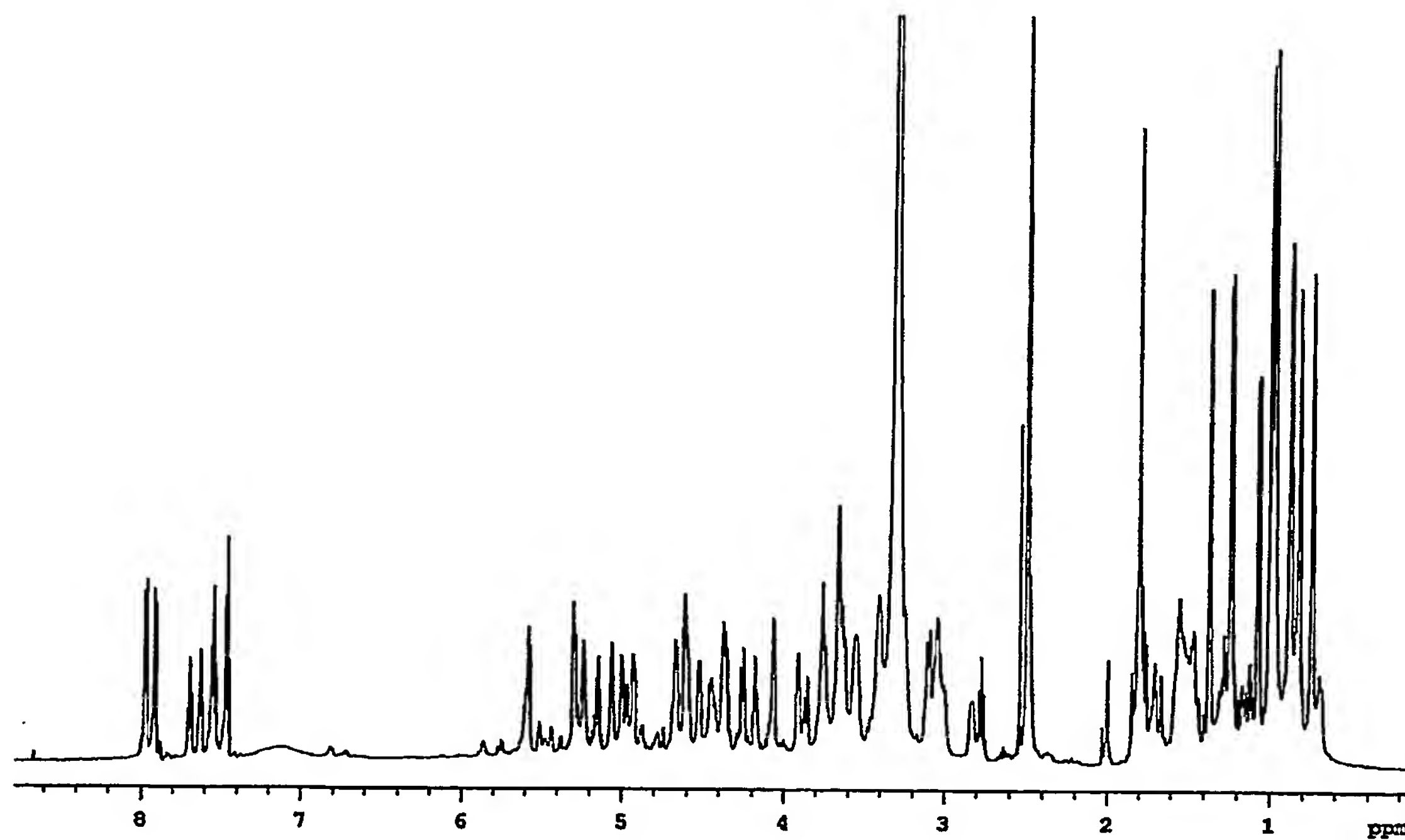
**FIG 40** - Separation of fraction F80.6 using a phenyl reverse phase column with the analytical separation (left) and the preparative separation (right).



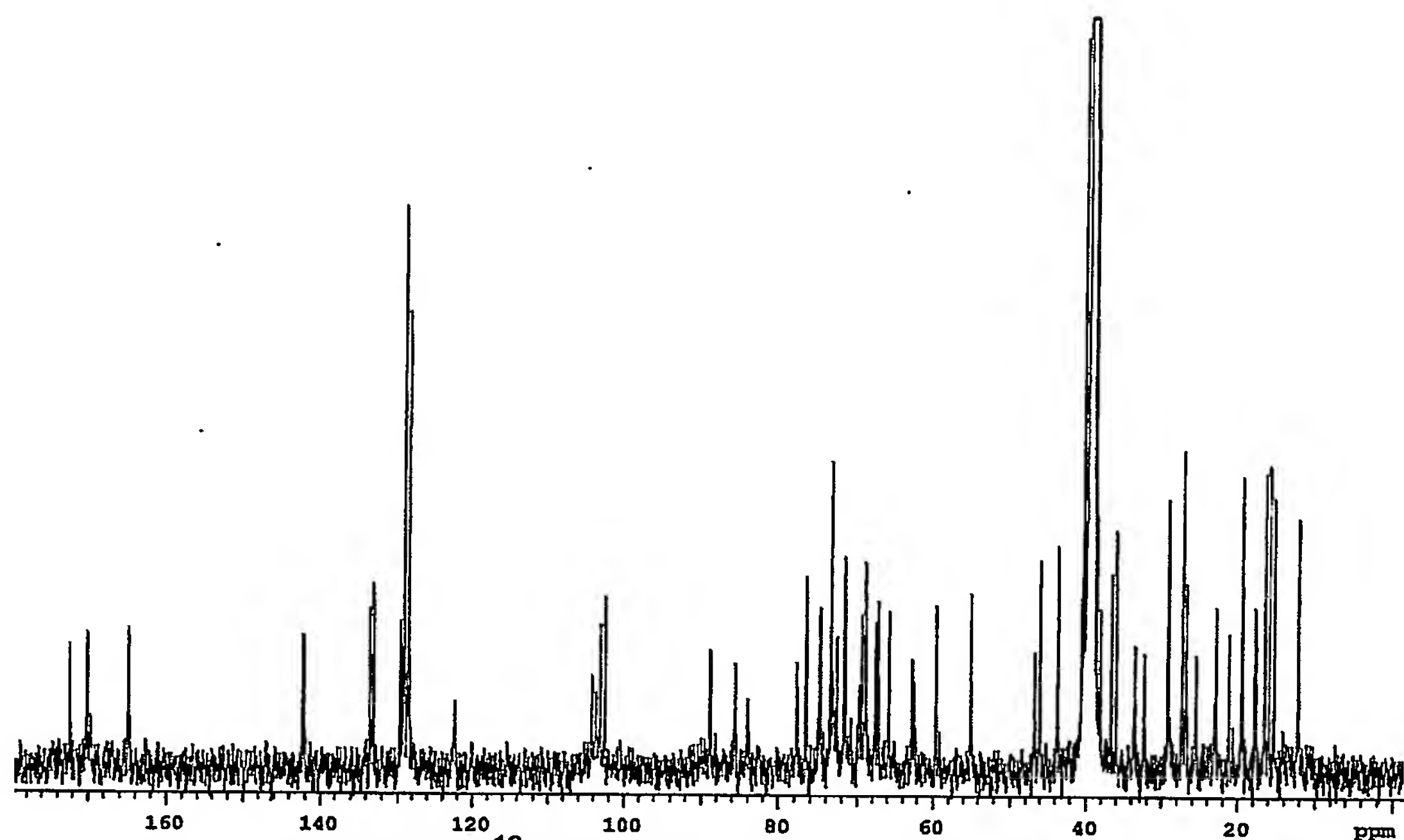
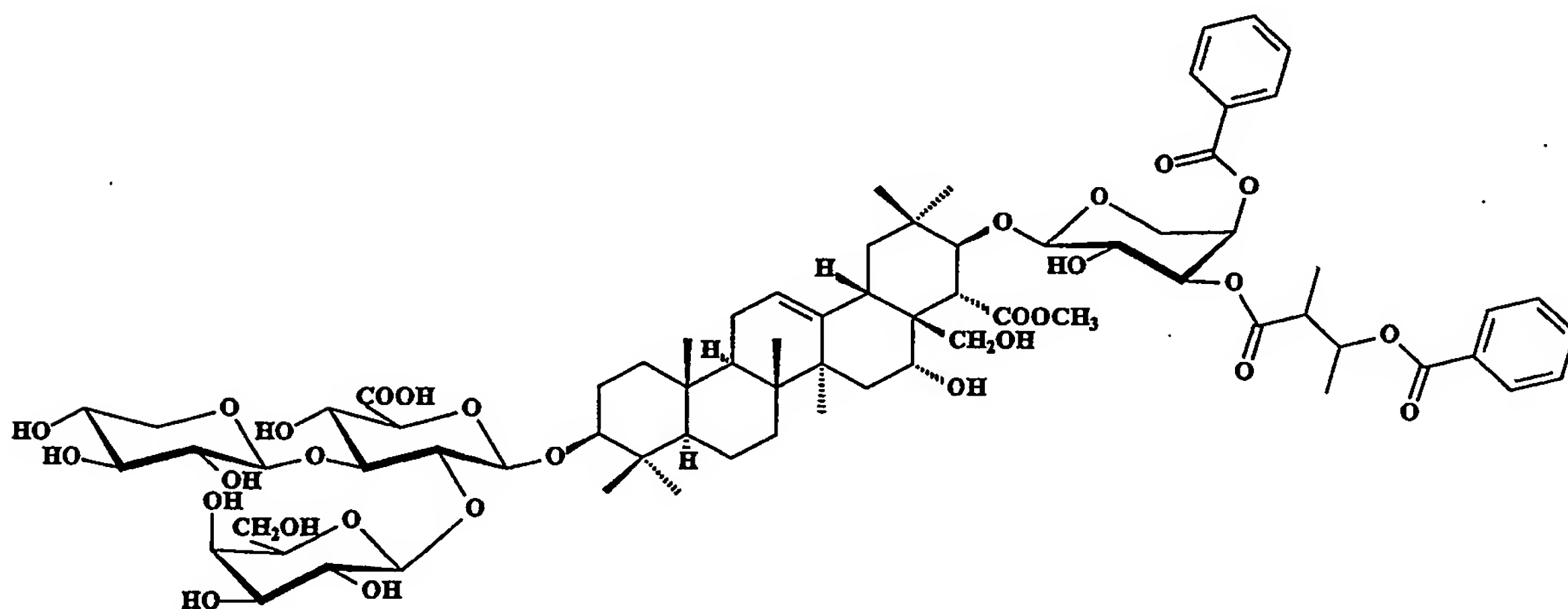
**FIG 41** - Standard sugars used for TLC



**FIG 42** - UV spectrum of F70.3.6

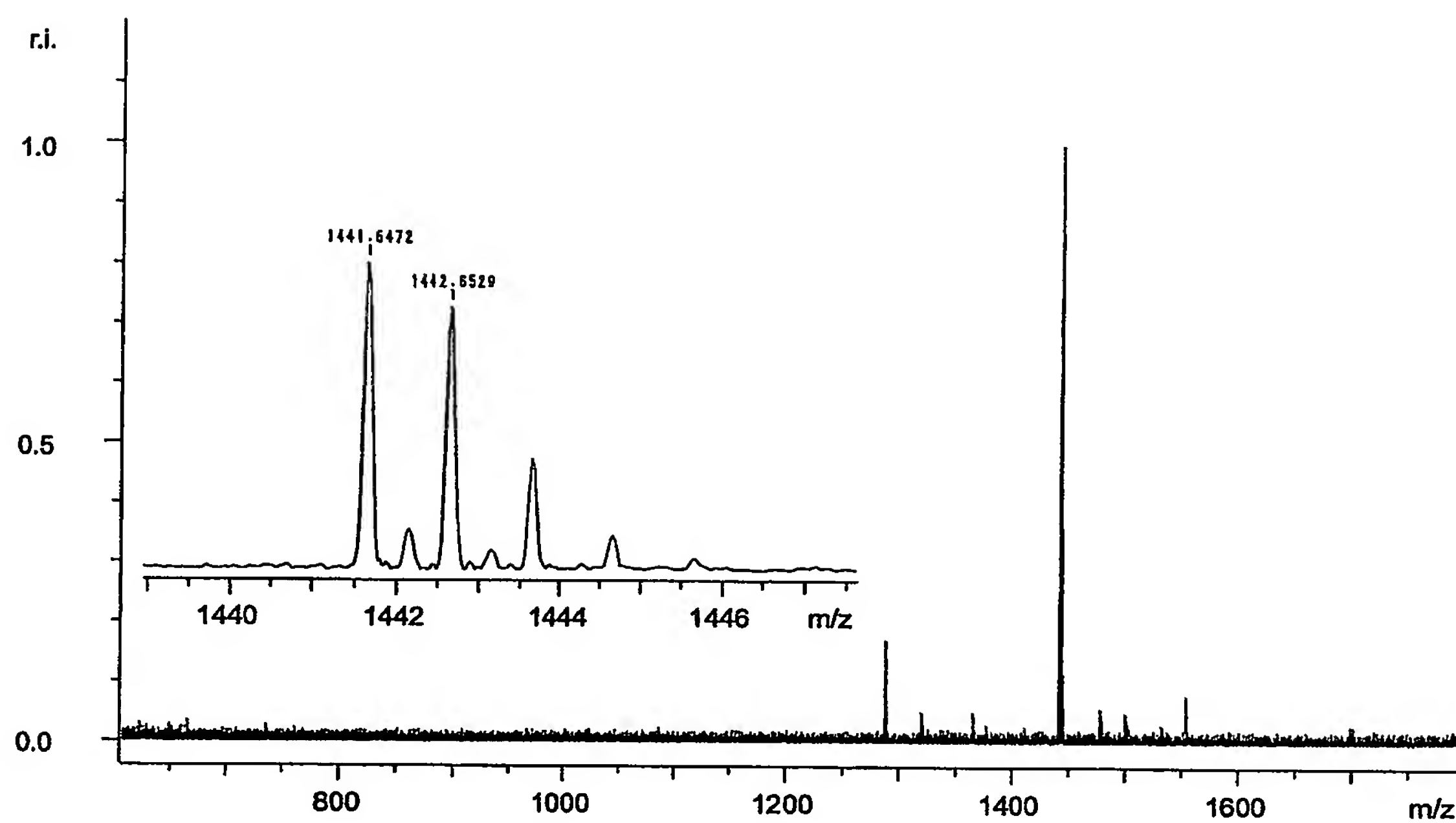
**21/35****FIG 43 - FTIR spectrum of F70.3.6****FIG 44 - <sup>1</sup>H-NMR for compound F70.3.6**

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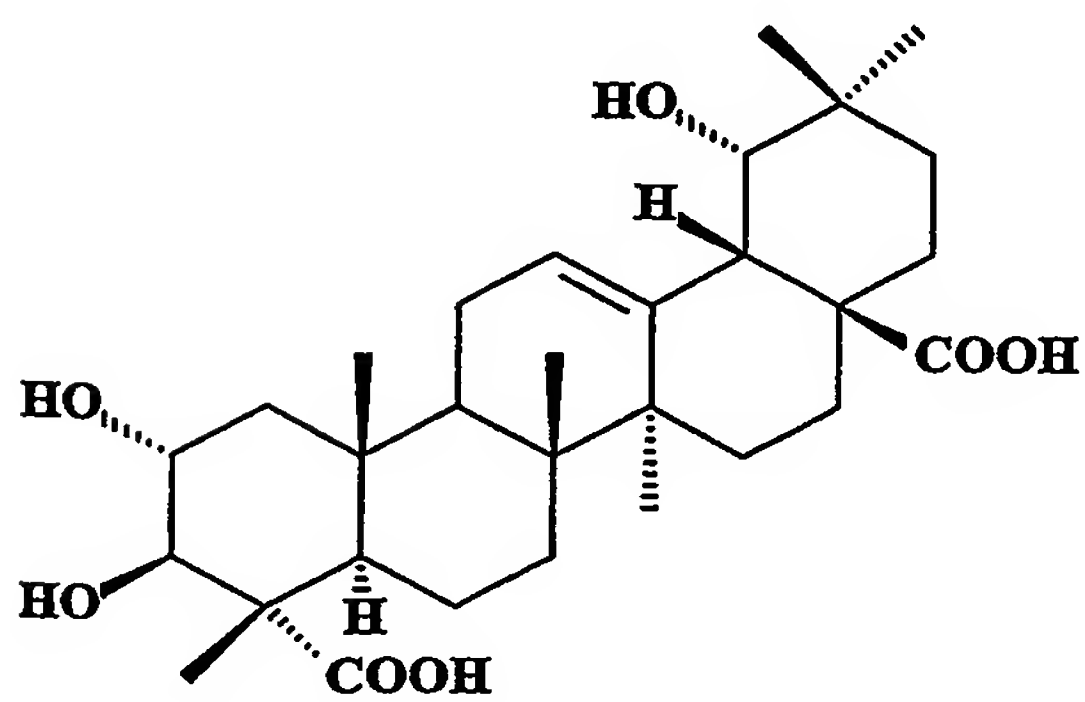
FIG 45 -  $^{13}\text{C}$ -NMR for compound F70.3.6

**FIG 46 - The complete assignment of F70.3.6**  
(3-O- $\beta$ -D-xylopyranosyl(1 $\rightarrow$ 3)-[ $\beta$ -D-galactopyranosyl(1 $\rightarrow$ 2)]- $\beta$ -D-glucuronopyranosyl-21-O-[3-(3-benzoyl-2-methylbutanoyl)-4-benzoyl- $\alpha$ -L-arabinopyranosyl]-22-O-acetyl barringtogenol C)

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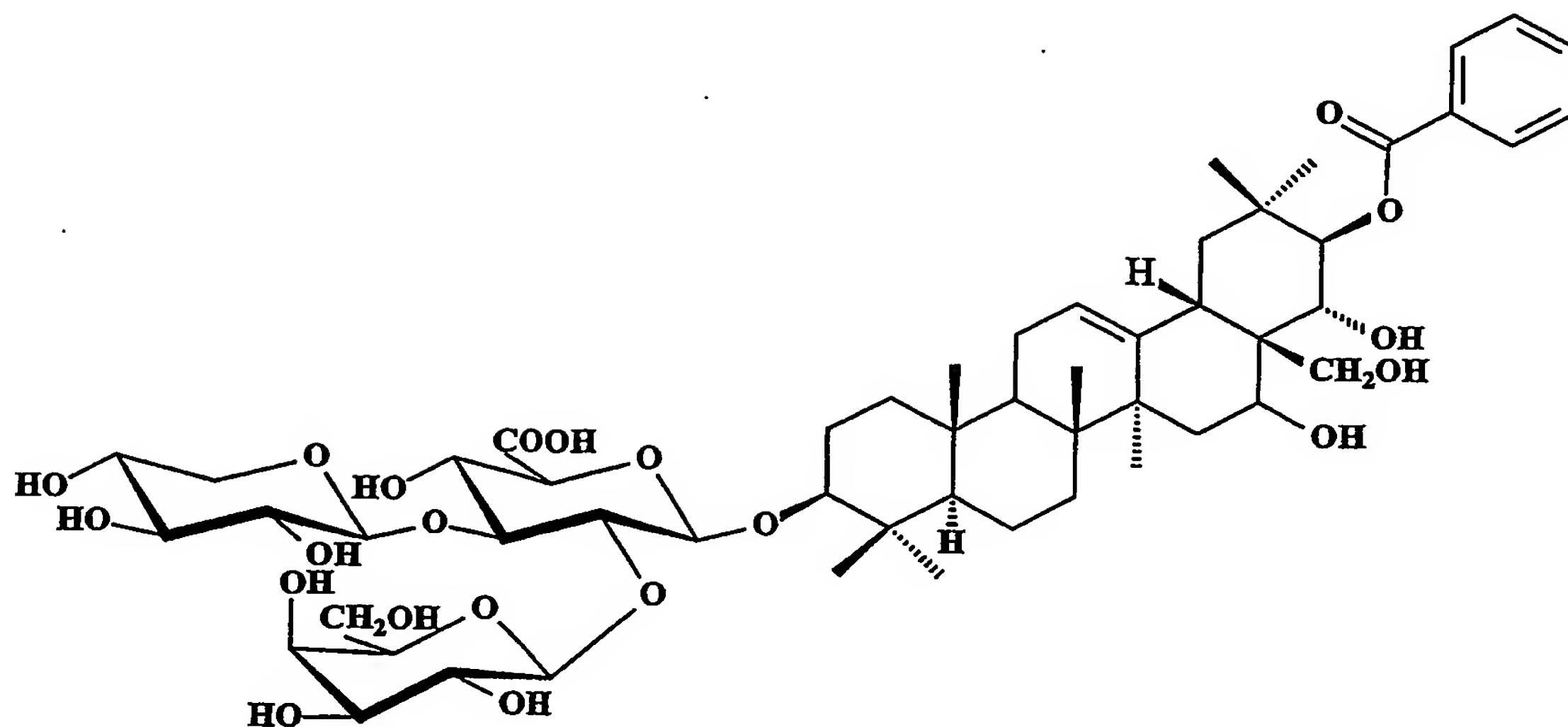


**FIG 47** - Negative ion HR-ESMS of F70.3.6 (insets show detail of molecular ion)



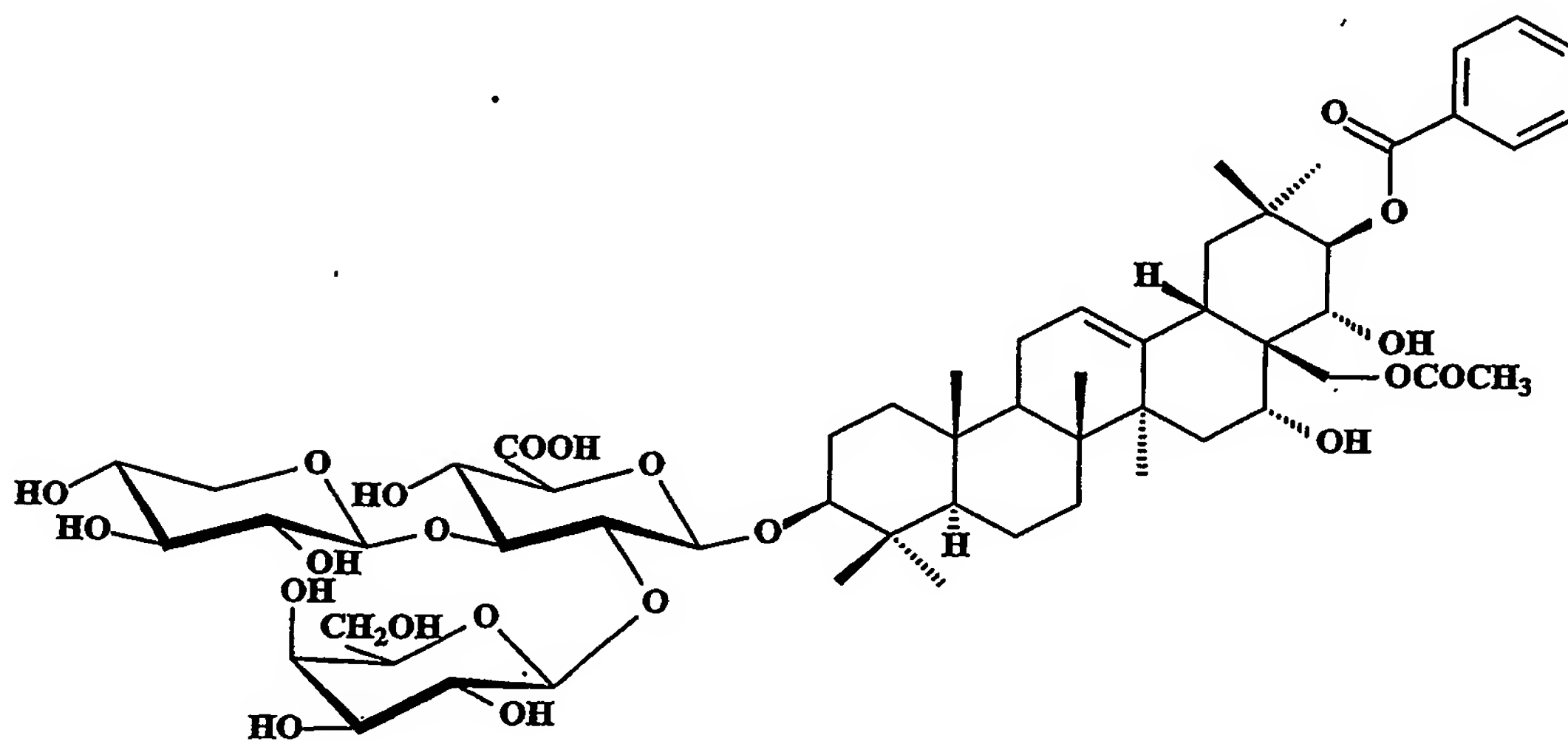
**FIG 48** - Compound F70.2.5.2  
(2 $\alpha$ , 3 $\beta$ , 19 $\alpha$ -trihydroxy-olean-12-ene-23,  
28-dioic acid)

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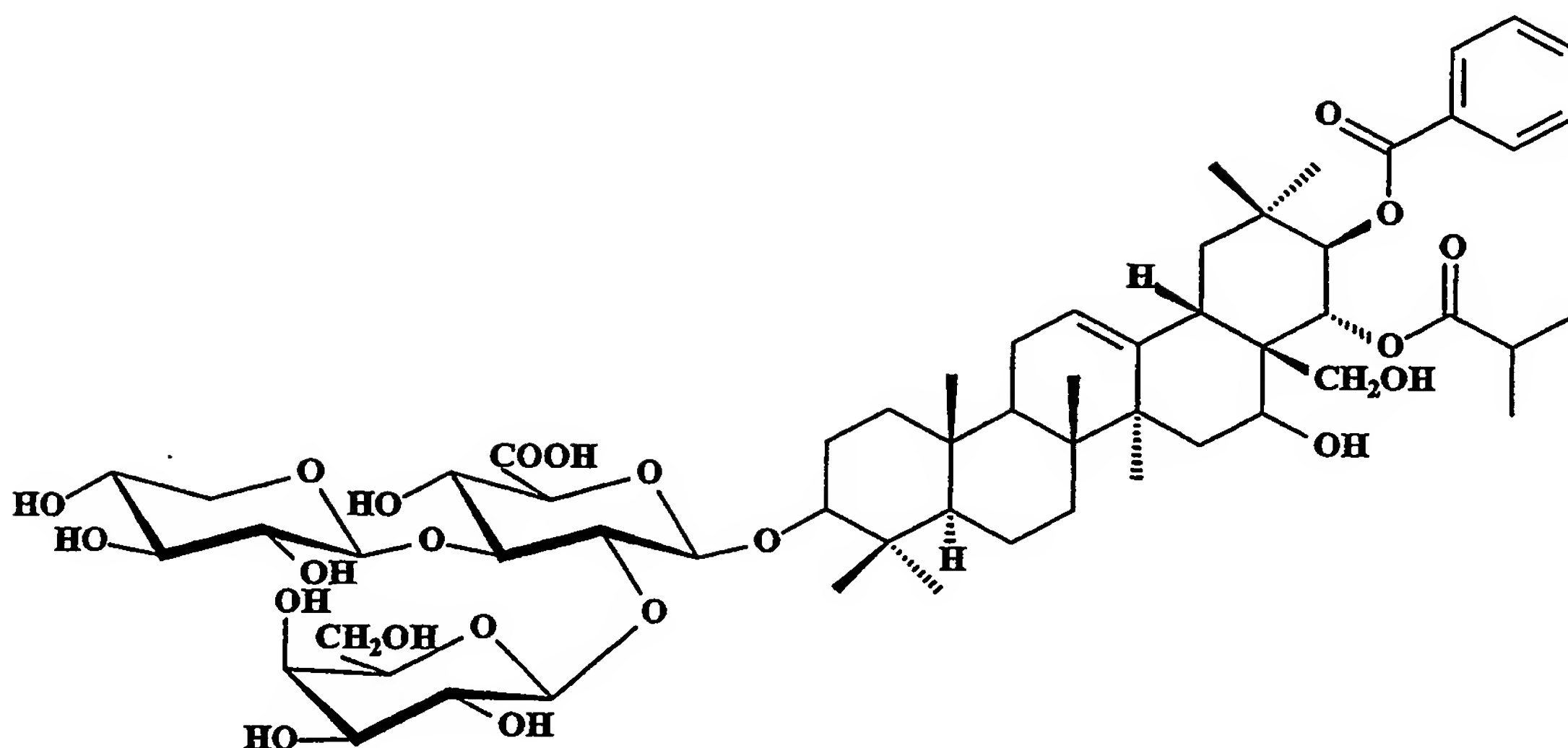
**FIG 49 - Compound F70.2.3.**  
*(3-O-β-D-xylopyranosyl(1→3)-[β-D-galactopyranosyl(1→2)]-β-D-glucuronopyranosyl-21-O-benzoyl barringtogenol C)*



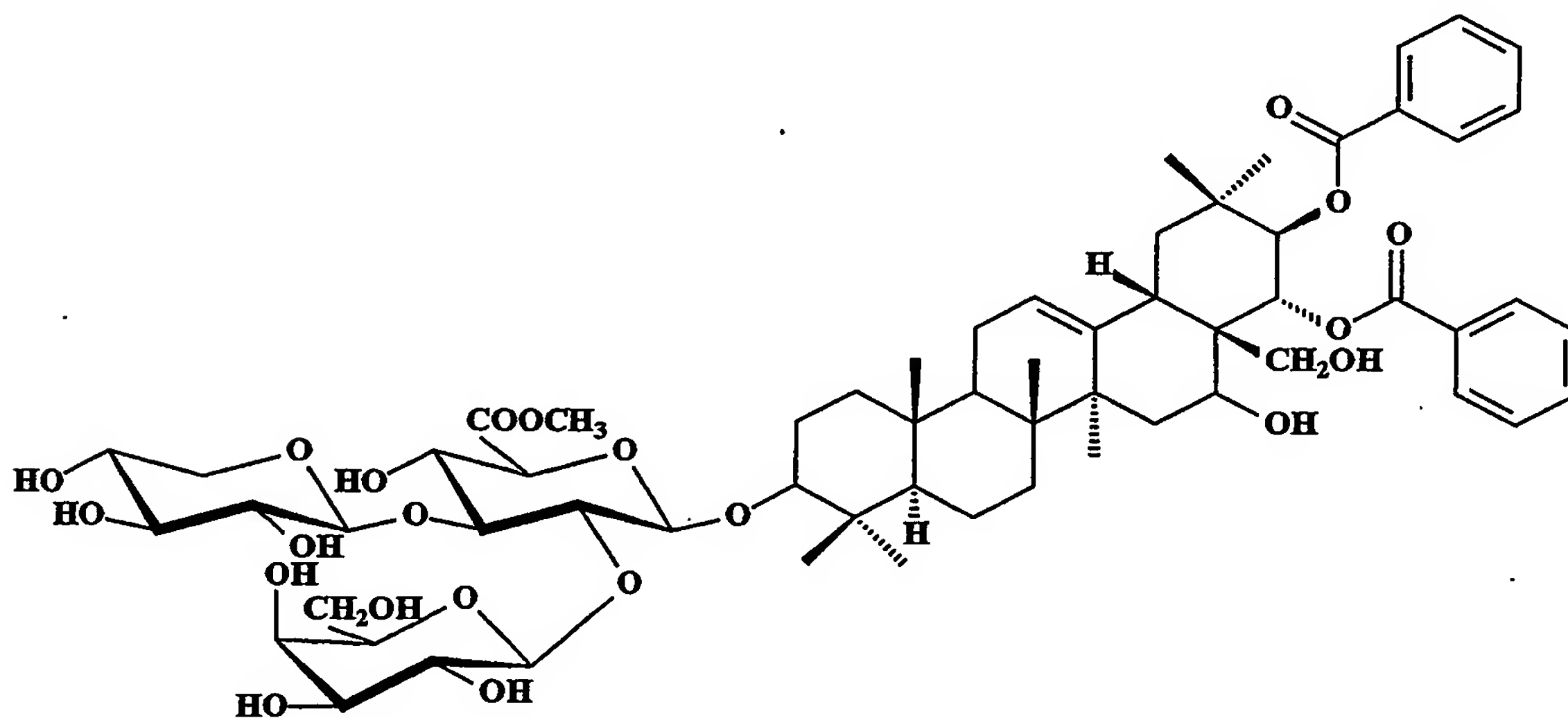
**FIG 50 - Compound F70.3.2**  
*3-O-β-D-xylopyranosyl(1→3)-[β-D-galactopyranosyl(1→2)]-β-D-glucuronopyranosyl-21-O-benzoyl-28-O-acetyl barringtogenol C)*



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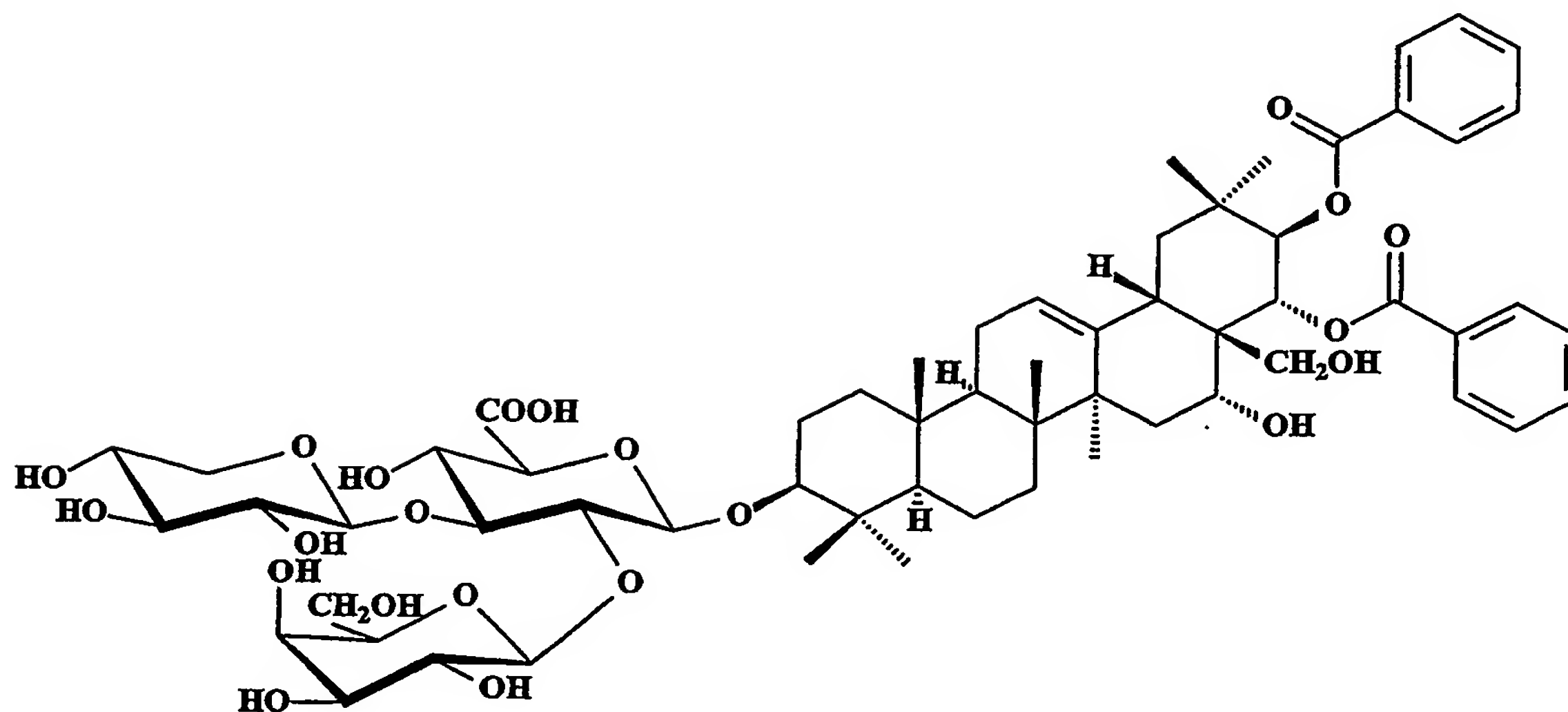


**FIG 51 - Compound F70.3.4.2**  
(3-O- $\beta$ -D-xylopyranosyl(1 $\rightarrow$ 3)-[ $\beta$ -D-galactopyranosyl(1 $\rightarrow$ 2)]- $\beta$ -D-glucuronopyranosyl-21-O-benzoyl-22-O-isobutyryl barringtogenol C)

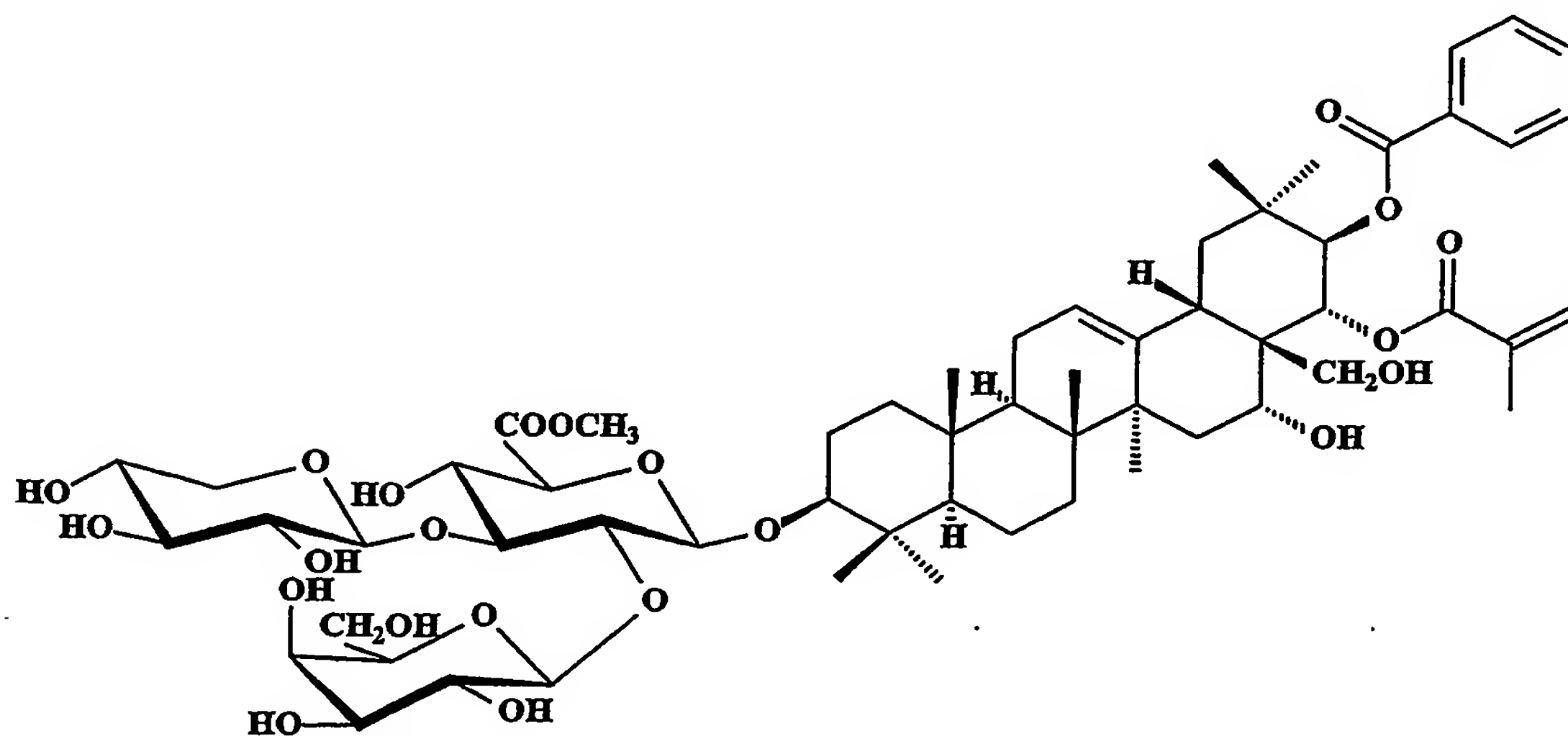


**FIG 52 - Compounds F70.4.3.5.2/F80.6.7**  
(3-O- $\beta$ -D-xylopyranosyl(1 $\rightarrow$ 3)-[ $\beta$ -D-galactopyranosyl(1 $\rightarrow$ 2)]- $\beta$ -D-methylglucuronopyranosyl-21,22-O-dibenzoyl barringtogenol C)

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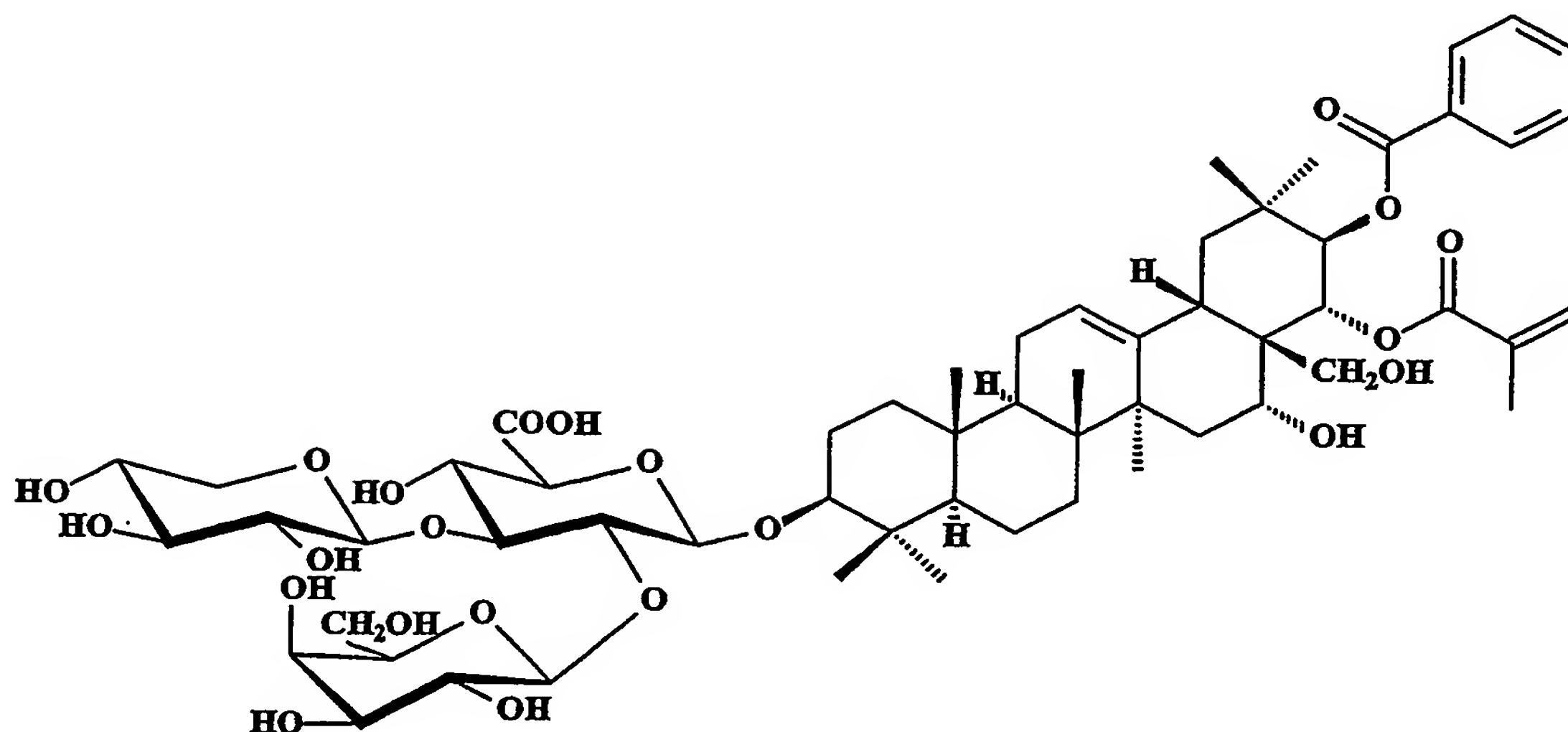


**FIG 53 - Compound F80.6.4/F70.4.2.4.2**  
(3-O-β-D-xylopyranosyl(1→3)-[β-D-galactopyranosyl(1→2)]-β-D-glucuronopyranosyl-21, 22-O-dibenzoyl barringtogenol C)

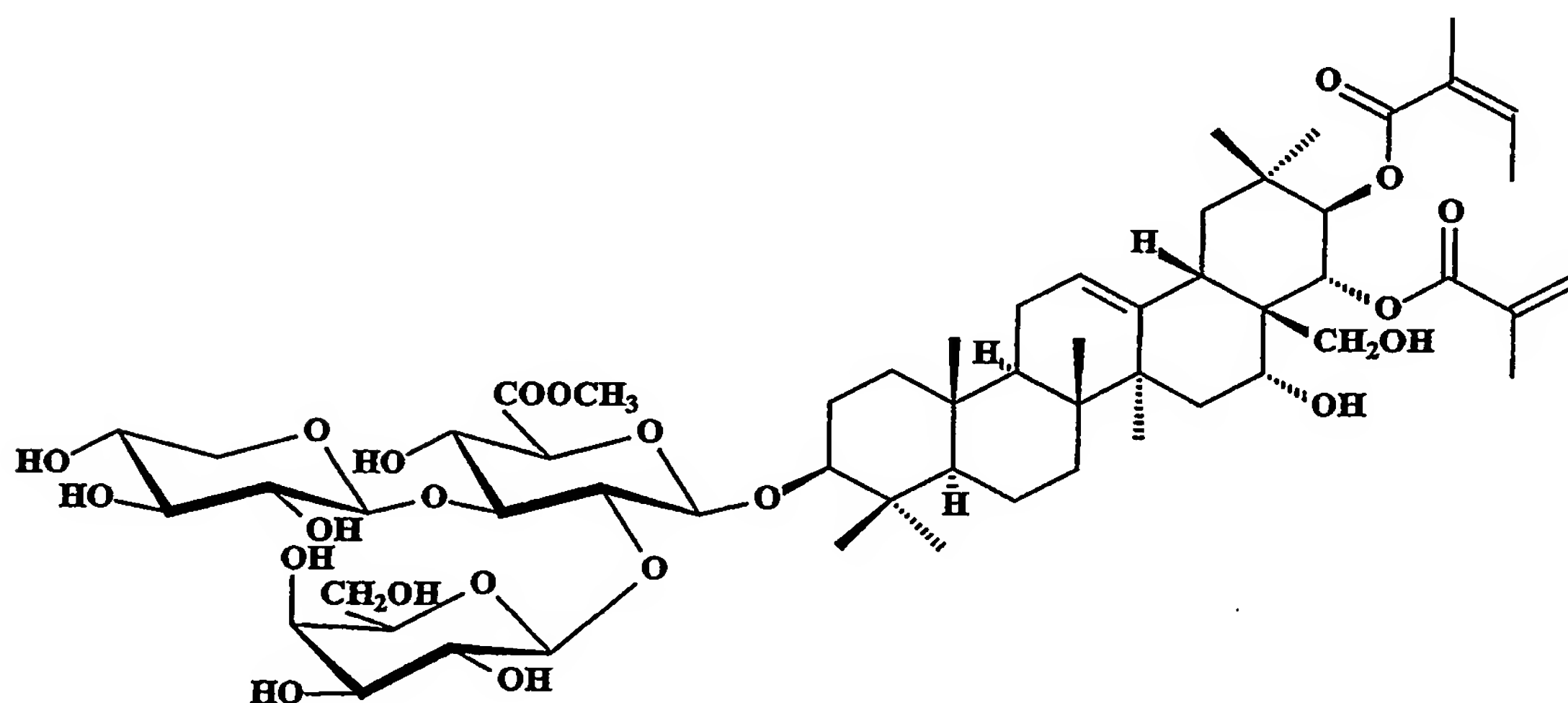


**FIG 54 - Compound F70.4.3.4.2/F80.6.6**  
(3-O-β-D-xylopyranosyl(1→3)-[β-D-galactopyranosyl(1→2)]-β-D-methylglucuronopyranosyl-21-O-benzoyl-22-O-tigloyl barringtogenol C)

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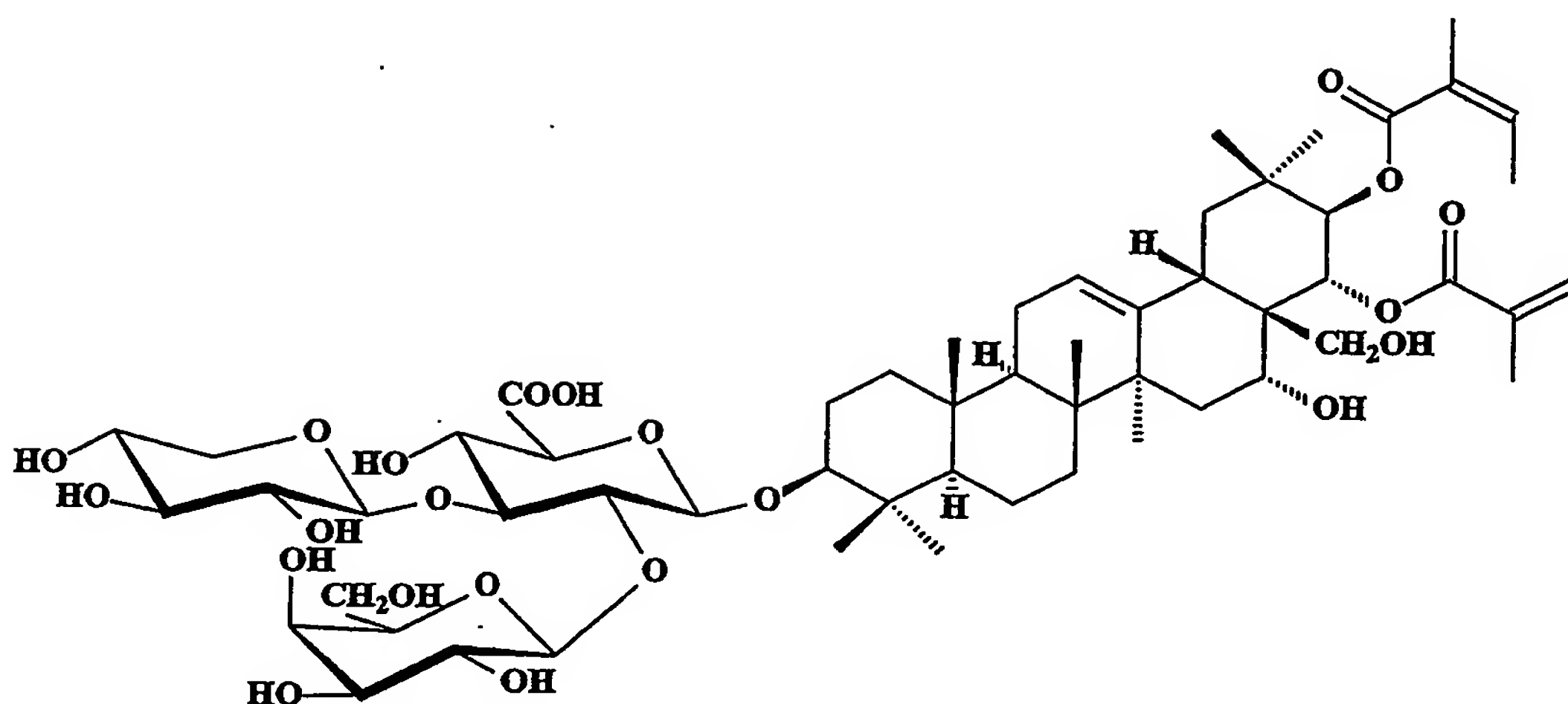


**FIG 55 - Compound F70.4.2.3/F80.6.3**  
(3-O- $\beta$ -D-xylopyranosyl(1  $\rightarrow$  3)-[ $\beta$ -D-galactopyranosyl(1  $\rightarrow$  2)]- $\beta$ -D-glucuronopyranosyl-21-O-benzoyl-22-O-tigloyl barringtonenol C)

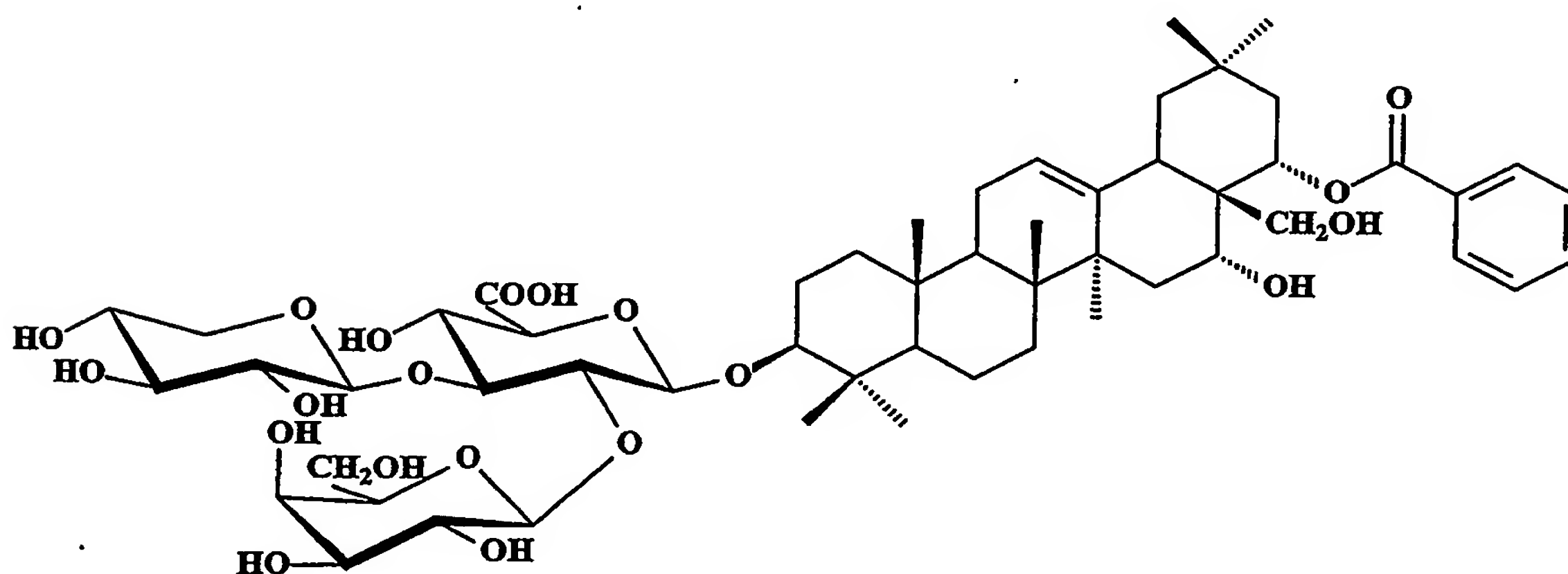


**FIG 56 - Compound F70.4.3.2.2**  
(3-O- $\beta$ -D-xylopyranosyl(1  $\rightarrow$  3)-[ $\beta$ -D-galactopyranosyl(1  $\rightarrow$  2)]- $\beta$ -D-methylglucuronopyranosyl-21,22-O-tigloyl barringtonenol C)

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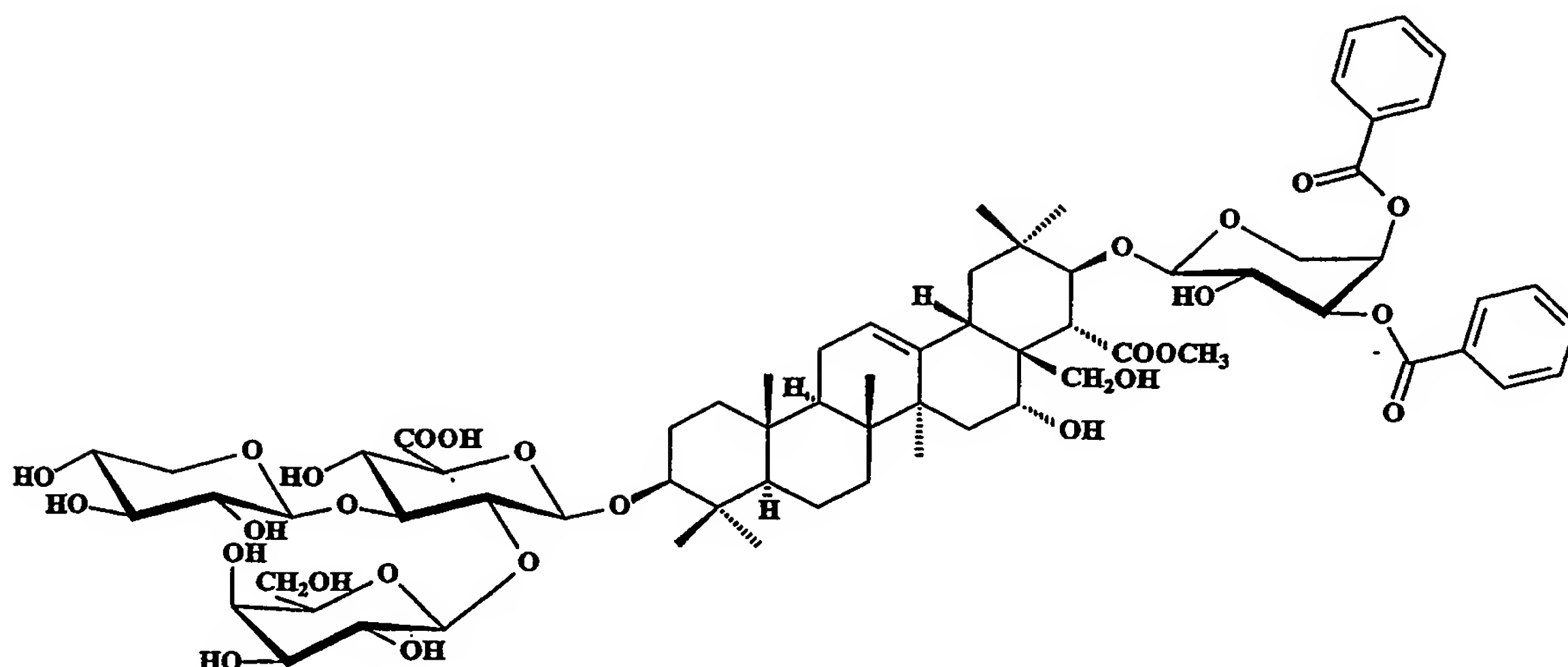


**FIG 57 - Compound F80.6.2**  
(3-O- $\beta$ -D-xylopyranosyl(1 $\rightarrow$ 3)-[ $\beta$ -D-galactopyranosyl(1 $\rightarrow$ 2)]- $\beta$ -D-glucuronopyranosyl-21,22-O-tigloyl barringtogenol C)

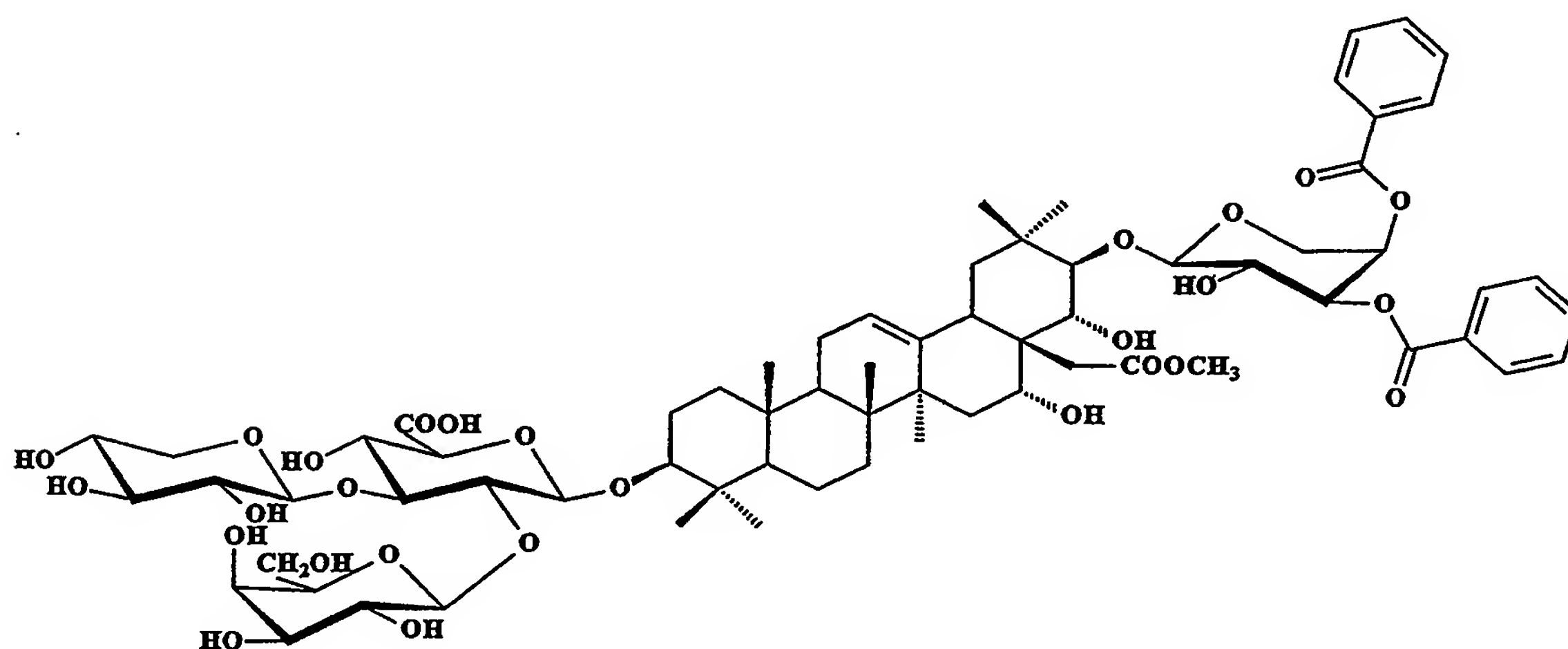


**FIG 58 - Compound F70.3.3.2.2b**  
(3-O- $\beta$ -D-xylopyranosyl(1 $\rightarrow$ 3)-[ $\beta$ -D-galactopyranosyl(1 $\rightarrow$ 2)]- $\beta$ -D-glucuronopyranosyl-22-O-benzoyl barringtogenol C)

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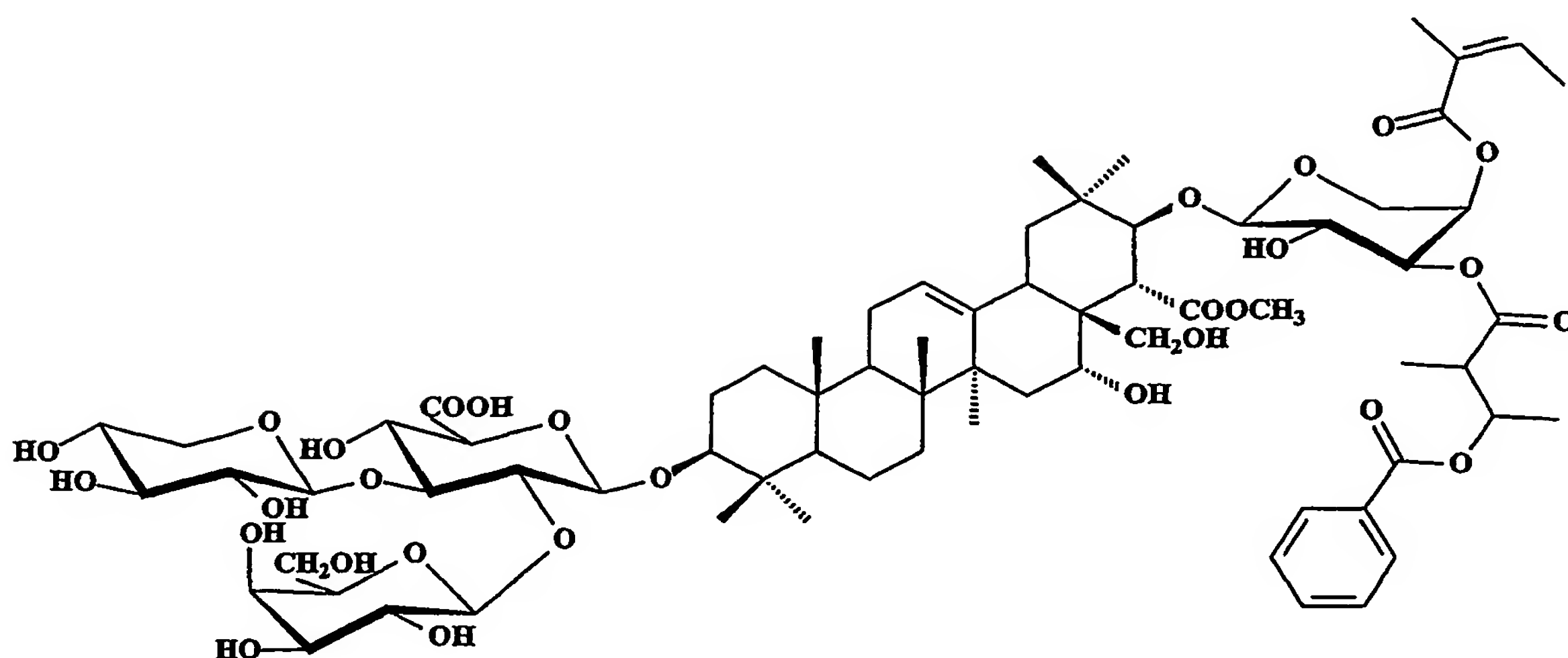
**FIG 59 - Compound F70.2.6.2**

(3-O- $\beta$ -D-xylopyranosyl(1 $\rightarrow$ 3)-[ $\beta$ -D-galactopyranosyl(1 $\rightarrow$ 2)]- $\beta$ -D-glucuronopyranosyl-21-O-[3,4-dibenzoyl- $\alpha$ -L-arabinopyranosyl]-22-O-acetyl barringtogenol C)

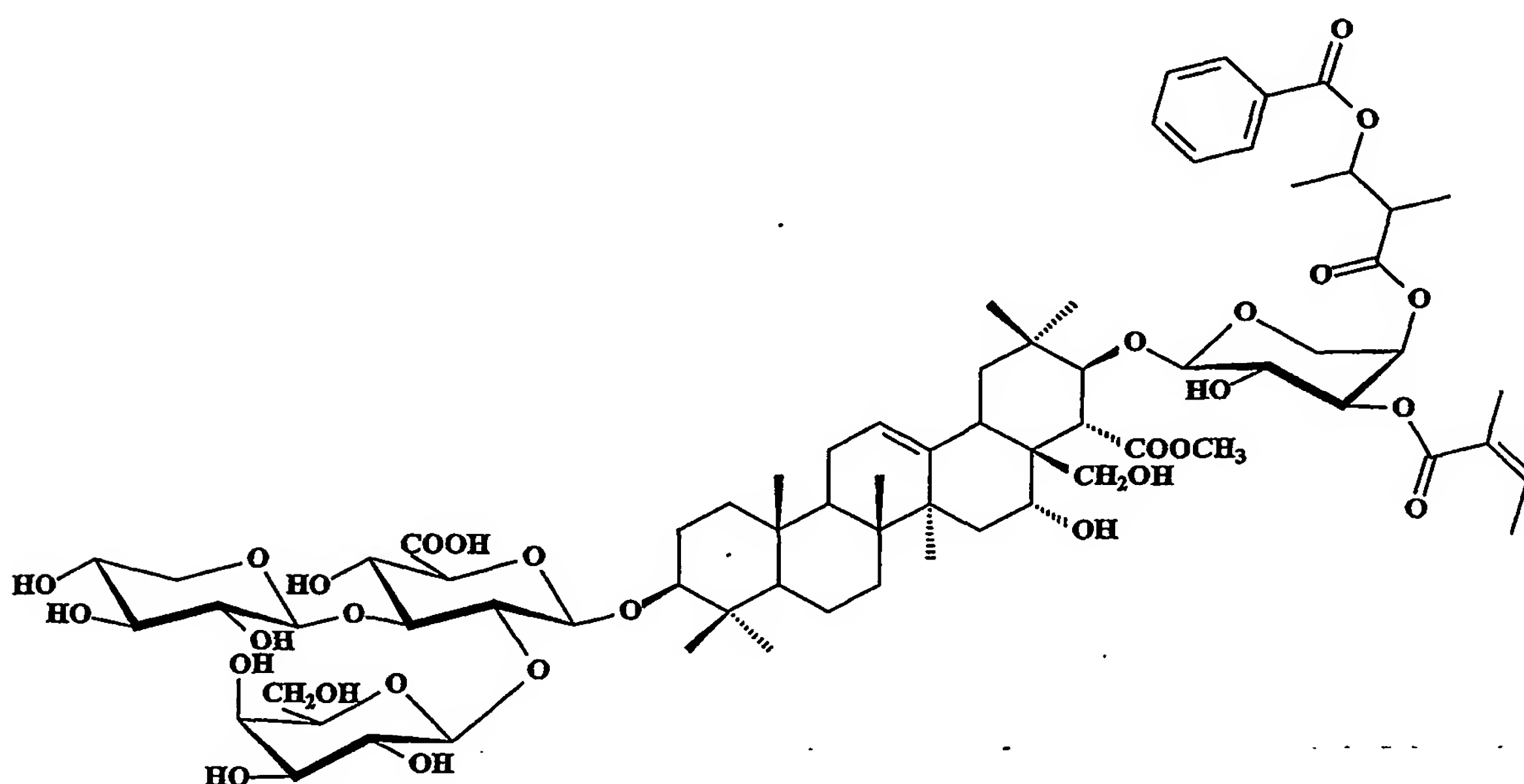
**FIG 60 - Compound F70.3.4.5**

(3-O- $\beta$ -D-xylopyranosyl(1 $\rightarrow$ 3)-[ $\beta$ -D-galactopyranosyl(1 $\rightarrow$ 2)]- $\beta$ -D-glucuronopyranosyl-21-O-[3,4-dibenzoyl- $\alpha$ -L-arabinopyranosyl]-28-O-acetyl barringtogenol C)

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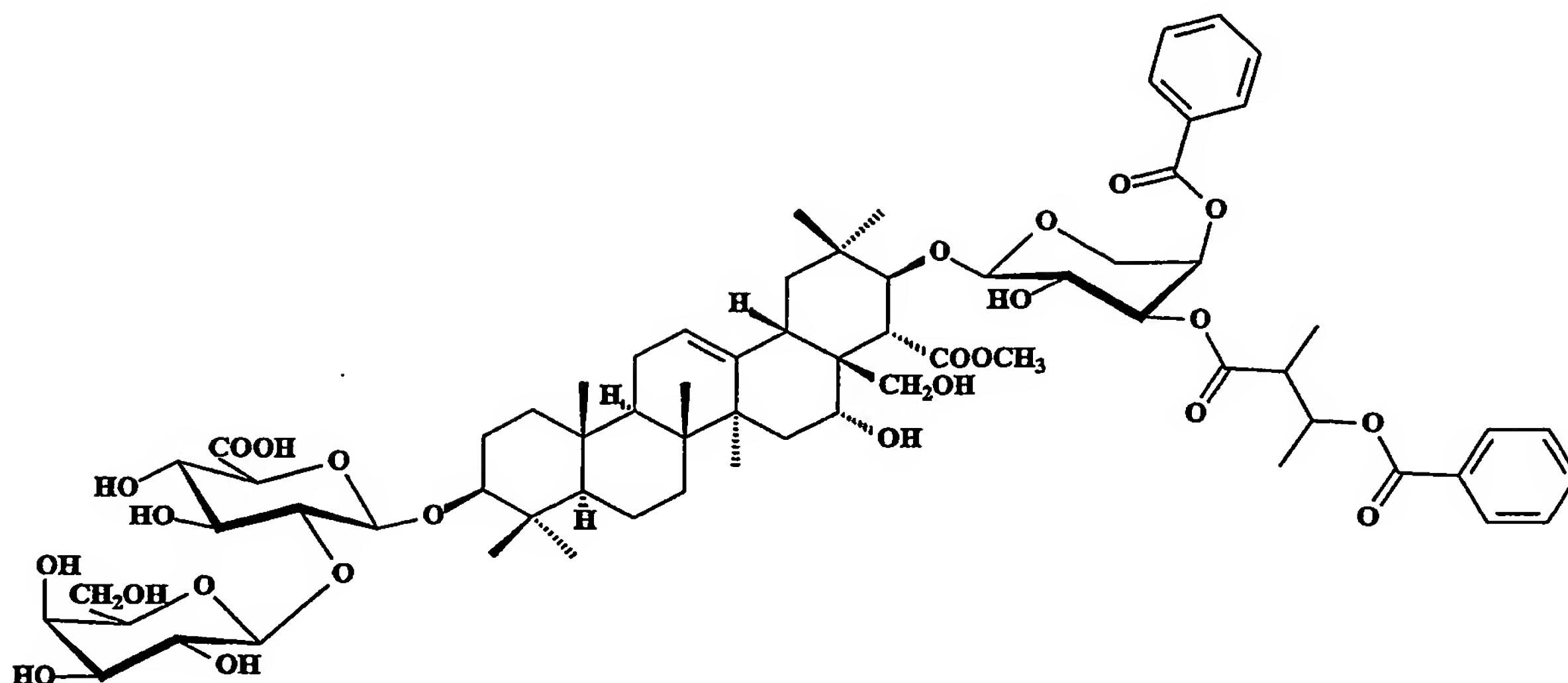
**FIG 61 - Compound F70.3.5a**

*(3-O-β-D-xylopyranosyl(1→3)-[β-D-galactopyranosyl(1→2)]-β-D-glucuronopyranosyl-21-O-[3-(3-benzoyl-2-methylbutyryl)-4-tigloyl-α-L-arabinopyranosyl]-22-O-acetyl barringtogenol C)*

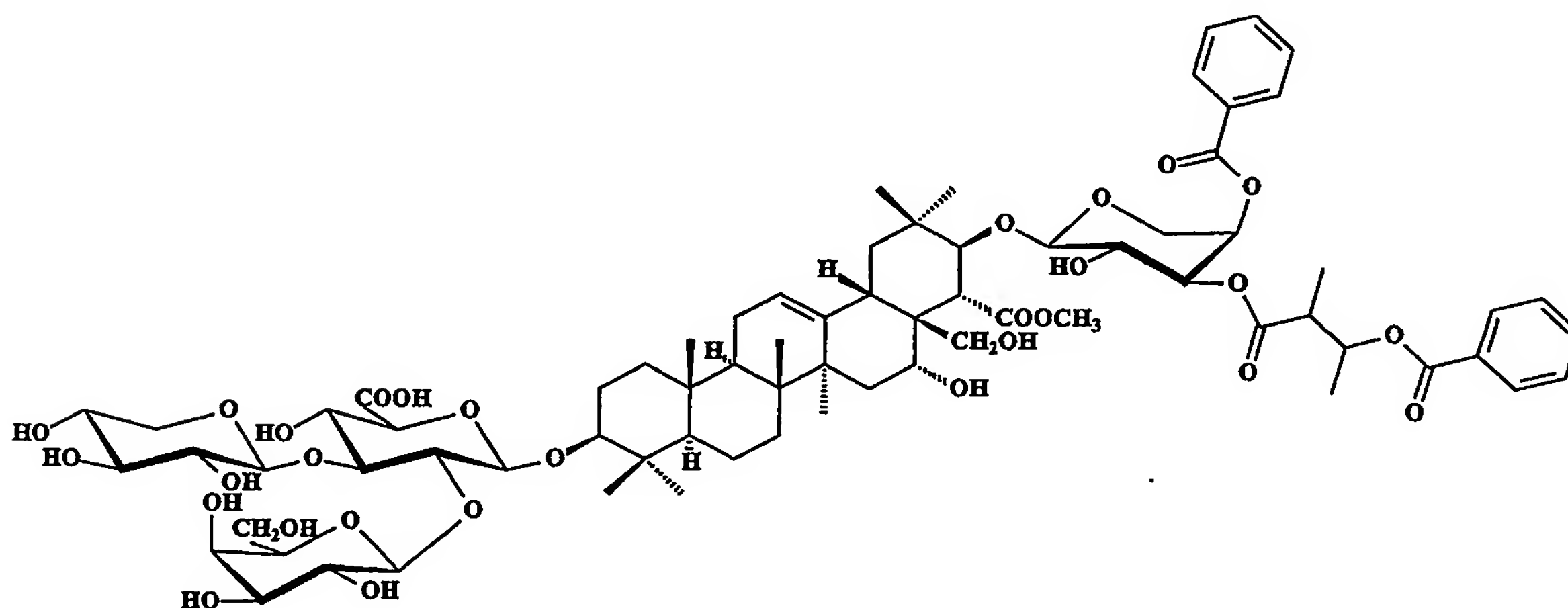
**FIG 62 - Compound F70.3.5b**

*(3-O-β-D-xylopyranosyl(1→3)-[β-D-galactopyranosyl(1→2)]-β-D-glucuronopyranosyl-21-O-[3-tigloyl-4-(3-benzoyl-2-methylbutyryl)-α-L-arabinopyranosyl]-22-O-acetyl barringtogenol C)*

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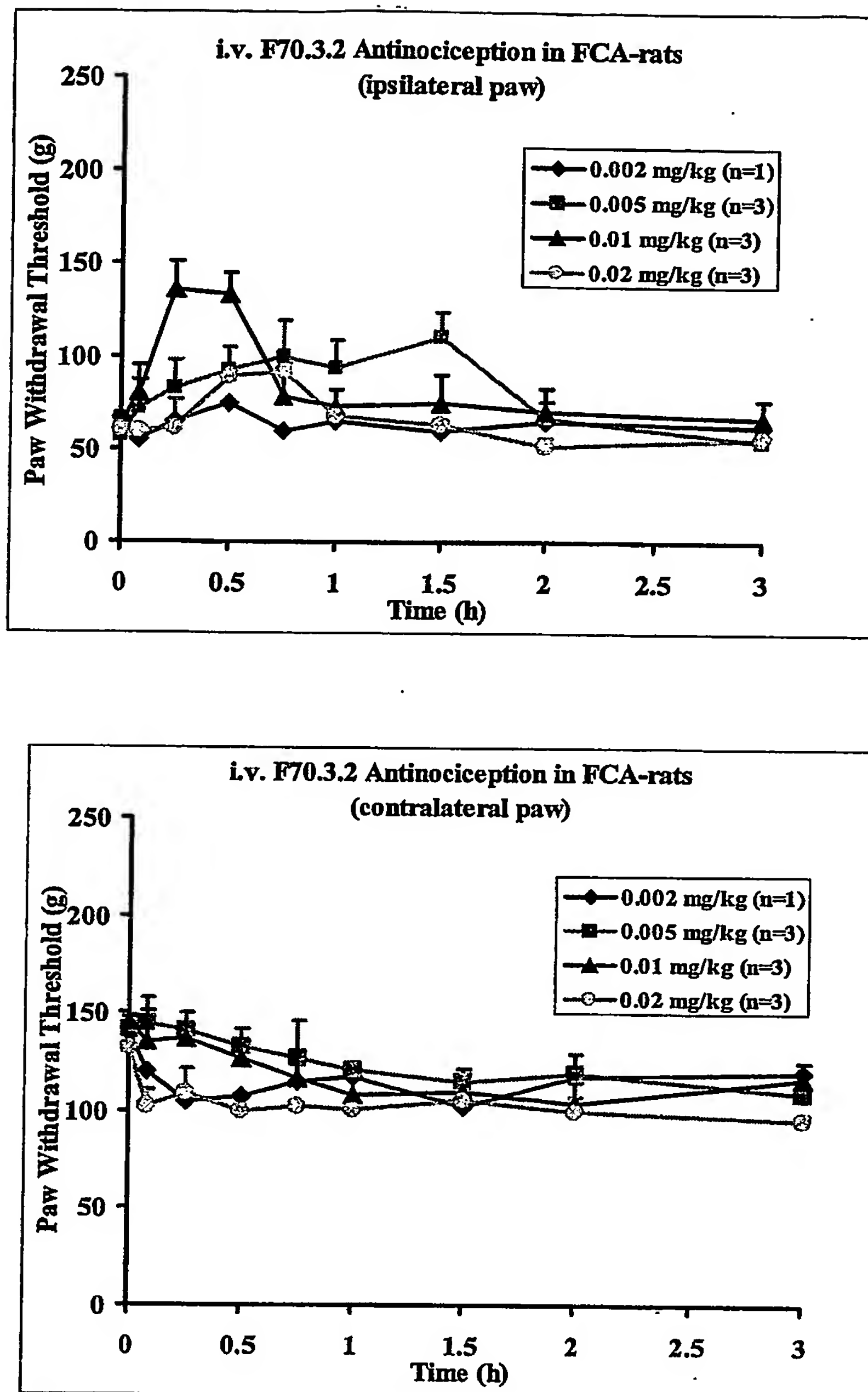
**FIG 63 - Compound F70.3.7.2**

(3-O-β-D-galactopyranosyl(1→2)-β-D-glucuronopyranosyl-21-O-[3-(3-benzoyl-2-methylbutyryl)-4-benzoyl-α-L-arabinopyranosyl]-22-O-acetyl barringtogenol C)

**FIG 64 - Compound F80.4.5.2/F80.5.2**

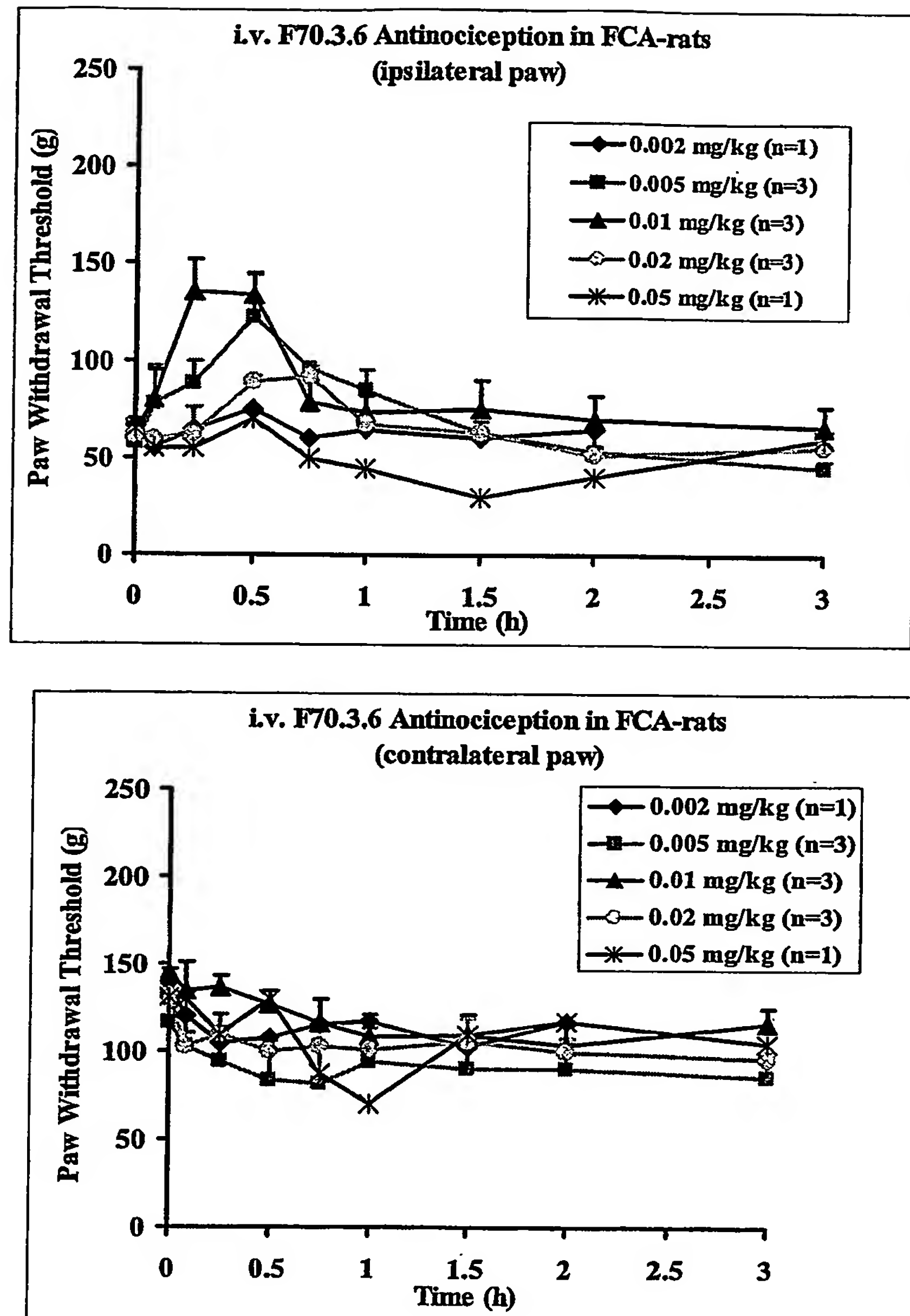
(3-O-β-D-xylopyranosyl(1→3)-[β-D-galactopyranosyl(1→2)]-β-D-glucuronopyranosyl-21-O-[3-(3-benzoyl-2-methylbutyryl)-4-benzoyl-α-L-arabinopyranosyl]-28-O-acetyl barringtogenol C)

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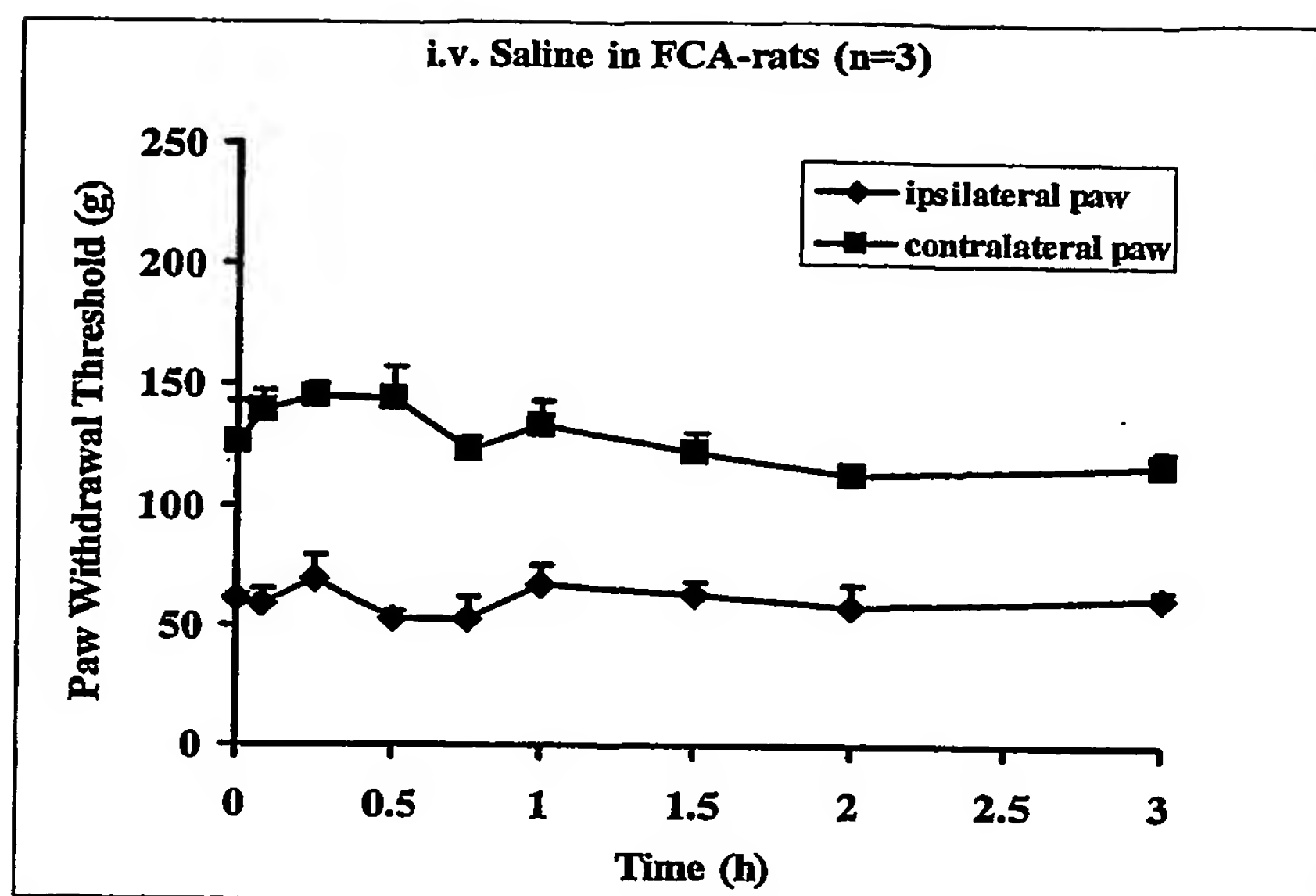




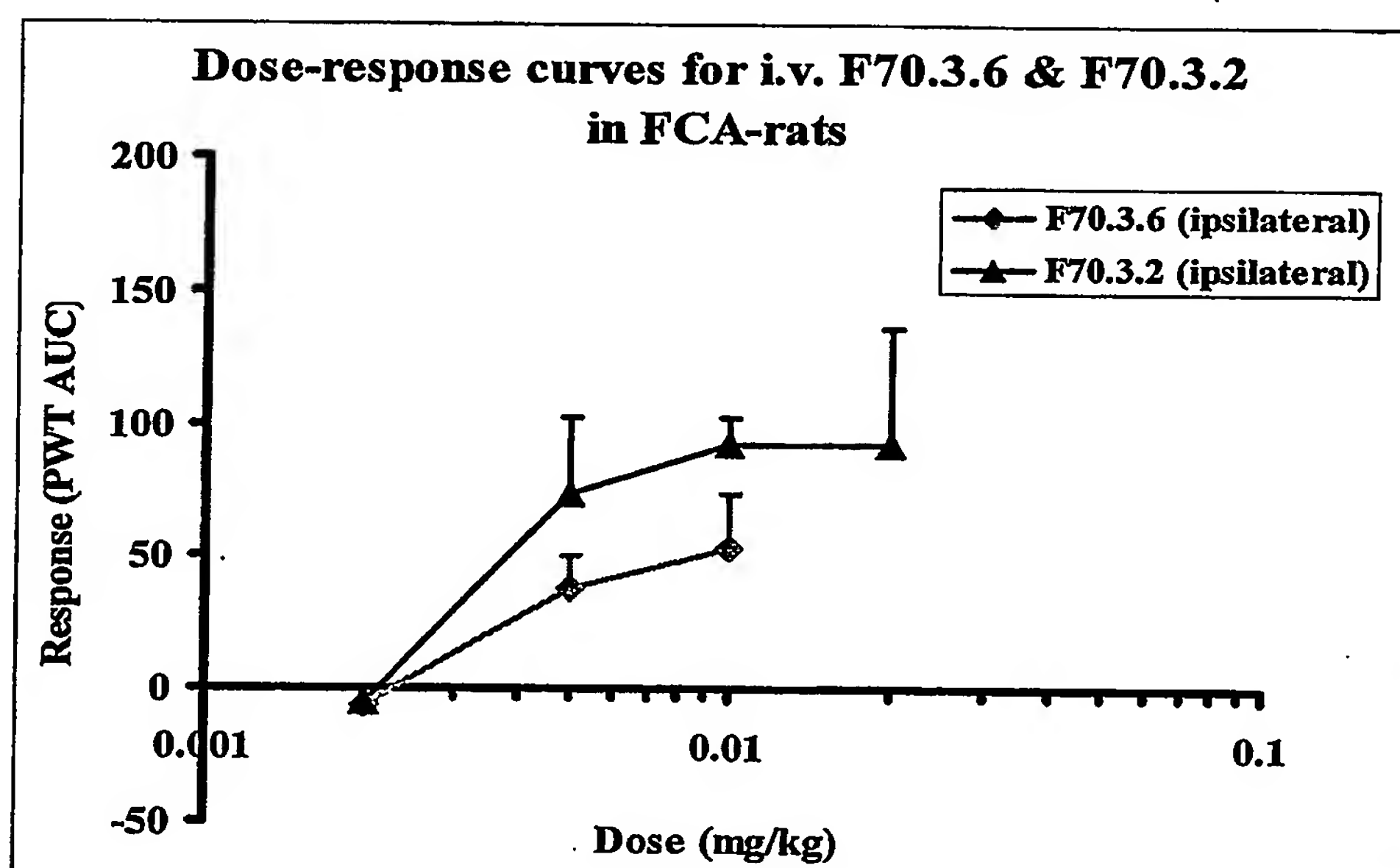
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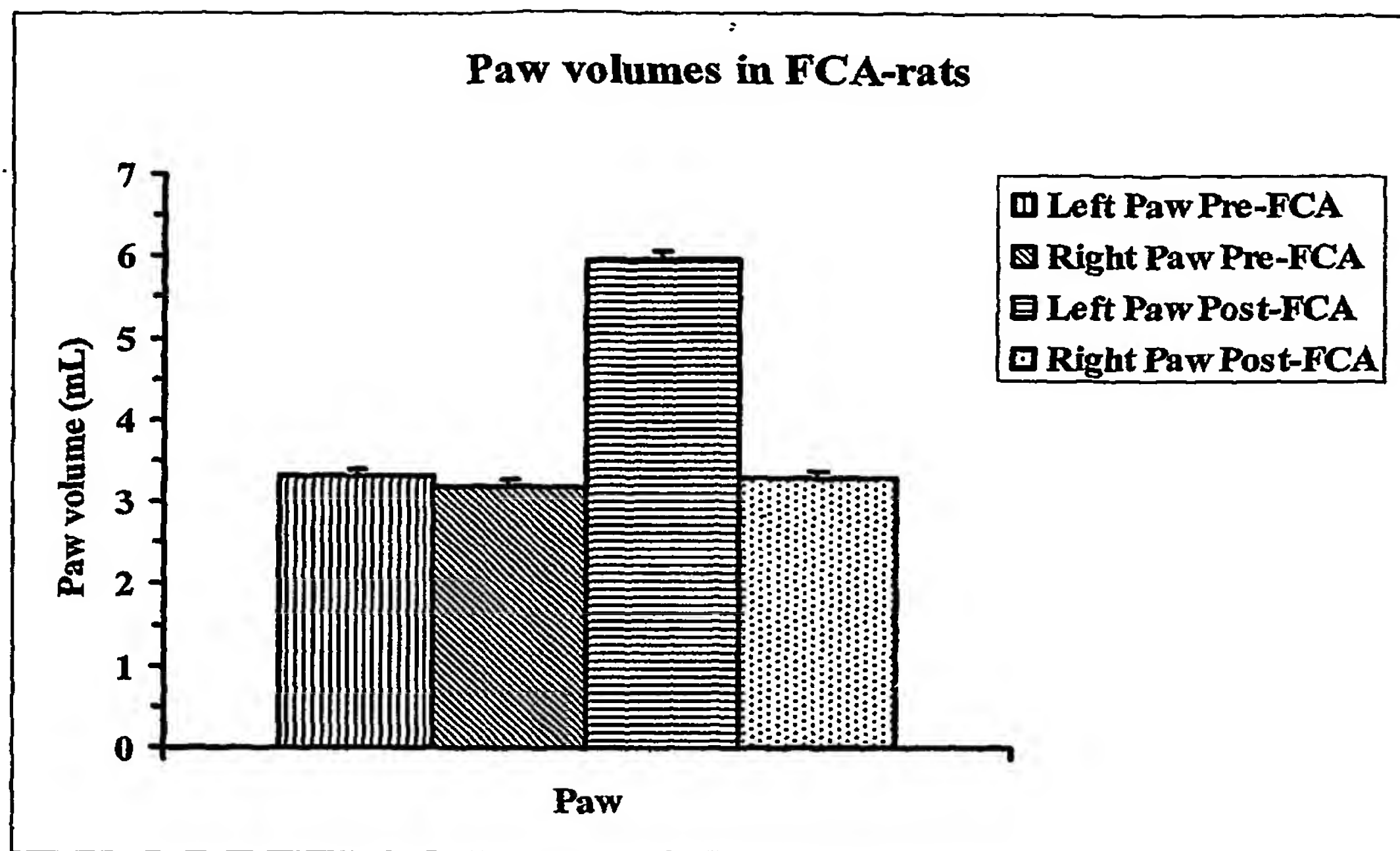


**FIG. 67:** is the mean ( $\pm$  SEM) paw withdrawal threshold versus time curve for the ipsilateral (inflamed) and the contralateral (non-inflamed) hindpaw in FCA-treated adult male Sprague-Dawley rats ( $n = 3$ ) that received a single i.v. bolus of saline.



**FIG. 68:** Mean ( $\pm$  SEM) dose-response curves for the antinociceptive effects of i.v. bolus doses of F70.3.2 and F70.3.6 in the ipsilateral hindpaws of FCA-rats.

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**FIG. 69** is a graph of the paw volume pre and post FCA treatment.